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Auto-oscillations in the Rates of Heterogeneous Catalytic Reactions

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Experimental data on the auto-oscillations in the rates of heterogeneous catalytic reactions are surveyed and the physicochemical principles of the origin of this phenomenon are examined. It is shown that the auto-oscillations can be due to a change in the properties of the catalyst under the influence of adsorbed reactants or reactants dissolved in a thin surface layer of the catalyst. Kinetic models of the reaction of hydrogen with oxygen on nickel and platinum catalysts, the phase plots of which contain limiting cycles, are examined in detail and models are presented for the auto-oscillations in the rate of reaction of oxygen with carbon monoxide on platinum catalysts. The importance of the auto-oscillations in the reaction rate for the development of the theory of heterogeneous catalysis is discussed.
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I. INTRODUCTION

A necessary condition for the occurrence of auto-oscillations is the presence in the system of a sufficiently strong feedback. It ensures the supply to the system of sufficient energy which is regulated by the movement of the oscillating system itself. The theory of bifurcations in dynamic systems constitutes the mathematical basis of the theory of auto-oscillations[1,2].

Heterogeneous catalytic systems have all the characteristic features of non-linear dynamic systems, so that under certain conditions there is a possibility of auto-oscillations in the rate of a heterogeneous catalytic reaction. Since the auto-oscillations are very sensitive to the structure and properties of the system, they are of considerable interest for the understanding of the detailed mechanism of chemical reactions and for the establishment of the general features of reactions involving various types of catalysis: homogeneous, enzymatic, and heterogeneous. The auto-oscillations in the rates of reaction in homogeneous chemical and biological systems have been vigorously studied recently and there are a number of fairly complete reviews[3-8]. This review gives an account of studies devoted to the auto-oscillations in heterogeneous catalytic systems alone.

II. EXPERIMENTAL DATA

The oxidation of carbon monoxide on platinum catalysts is one of the first heterogeneous catalytic systems where auto-oscillations in the reaction rate were observed in the kinetic

region. This reaction has been studied[9] in a flow-circulation apparatus; the catalyst consisted of a platinum mesh prepared from wire 0.04 mm in diameter and having 3600 apertures per square centimetre. The reaction mixtures contained a large excess of air. At very low carbon monoxides pressures in air stable stationary states were observed in the system and the reaction was of second order with respect to carbon monoxide. With increase of carbon monoxide pressure, stable oscillations appeared. If the partial pressure of carbon monoxide rose, the amplitude and frequency of the oscillations increased, the average rate of reaction reaching a maximum. A further increase in the partial pressure of carbon monoxide led to a sharp fall of the rate of reaction and to the disappearance of the oscillations.

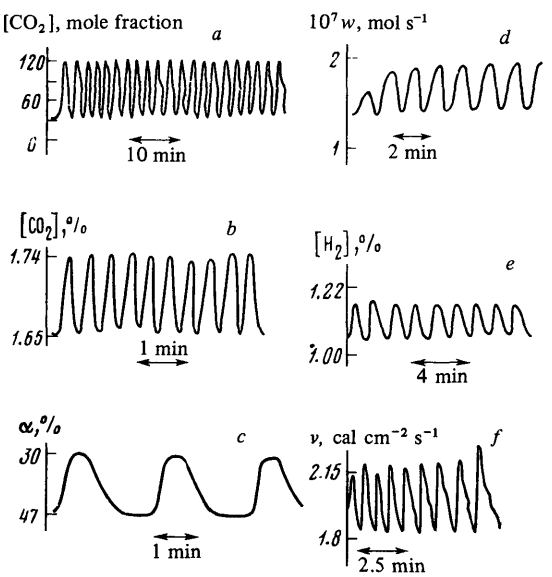


Figure 1. The overall form of the auto-oscillating processes in various heterogeneous catalytic systems: *a*) auto-oscillations in the rate of oxidation of carbon monoxide on a porous grain of platinised γ-alumina (180 °C; 1% CO; air)[10]; *b*) auto-oscillations in the rate of oxidation of CO on a Pt catalyst deposited on α-Al_2O_3;[11] *c*) auto-oscillations in the rate (degree of conversion α) of oxidation of CO on a Pt foil catalyst in an ideal mixing reactor (239 °C; 1.08% CO; air)[14]; *d*) auto-oscillations in the rate (*w*) of oxidation of hydrogen on a nickel foil (245 °C; 0.8% O_2; 99% H_2);[55] *e*) auto-oscillations in the rate of oxidation of hydrogen on a platinum wire (221 °C; 3.48% H_2; air)[53]; *f*) auto-oscillations in the rate of heat evolution in the oxidation of ethylene on a platinum wire (390 °C; 2% C_2H_4; 98% O_2).[24]

A similar dependence of the rate of reaction of carbon monoxide with oxygen on the carbon monoxide concentration in the gas phase was observed in another study[10] of this reaction on a catalyst grain containing 0.3% Pt deposited on γ-Al_2O_3. The reaction was carried out in a flow reactor in a stream of air containing small amounts of carbon monoxide. Fig. 1*a* illustrates the stable oscillations of the reaction rate observed in the region of the rate maximum. The period of the oscillations was several minutes. As in the oxidation of carbon monoxide on the platinum mesh, the amplitude of the oscillations increased with increase of the CO concentration in the initial mixture. As the catalyst temperature rose, the frequency of the oscillations increased and their amplitude fell. Above 250 °C the oscillation vanished. The authors[10] noted the high sensitivity of the characteristics of the oscillations to the properties of the catalyst. On passing from one catalyst grain to another, a change in the amplitude and period of the oscillations was noted.

McCarthy et al.[11] also investigated the reaction of CO and O_2 on a deposited catalyst containing 0.035% of platinum. At catalyst temperatures below 260 °C the dependence of the rate of reaction on the carbon monoxide concentration which they observed had a maximum corresponding to less than 0.5% of carbon monoxide in oxygen†; in the region of this maximum the author observed oscillations in the rate of reaction with a period of the order of 20 s (Fig. 1*b*).

In the study of the influence of the adsorption of carbon monoxide in oxygen on the contact potential difference (CPD) between the platinum electrode and the silicon reference electrode[12] a sharp change of CPD was noted for [CO] = 2%. The authors[12] showed that the maximum in the rate of reaction of CO with O_2 at 200 °C corresponds to this composition of the reaction mixture. In order to observe the auto-oscillations in the rate of this reaction, the authors employed two methods. In the first case CO was oxidised on a platinum wire 0.03 mm in diameter. The amplitude of the oscillations in the resistance of the wire induced by the oscillations in the rate of reaction corresponded to a change in the catalyst temperature by 5 °C. The oscillations were observed in a stream of oxygen containing 2% of carbon monoxide. In the second method CO was oxidised on an electrode made of *n*-type silicon on which a thin layer (100 Å) of platinum had been deposited. At 170 °C and [CO] = 1% the authors[12] observed oscillations in the photocurrent with a period of ~20 s, induced by the oscillations in the composition of the adsorbed layer in the oxidation of carbon monoxide on the platinum catalyst. It has been shown[13] that the amplitude of the oscillations reaches a maximum when the reactants distributed on the catalyst surface are in stoichiometric proportions.

The reaction of CO with O_2 on a platinum foil has been investigated[14]. It was carried out at atmospheric pressure in the temperature range 200–250 °C in a flow reactor free from temperature and concentration gradients. The authors investigated the dependence of the degree of conversion of carbon monoxide on the flow rate of the reaction mixture. The carbon monoxide concentration in air was varied from 1 to 4%. Depending on the experimental conditions, the establishment of either stable stationary states or auto-oscillations in the reaction rate was observed (Fig. 1*c*). The amplitude and period of the auto-oscillations increased with decrease in the degree of conversion at a constant CO pressure in the initial mixture. An analogous increase of the period and amplitude of the oscillations was observed with increase of the CO concentration in the initial mixture. As the temperature rose, the period and amplitude of the oscillations fell.

Virtually simultaneously with the auto-oscillations in the rate of oxidation of carbon monoxide on platinum catalysts, auto-oscillations were observed in the reaction of hydrogen with oxygen on a nickel foil[15,16] (Fig. 1*d*). The temperature

†Here and henceforth the concentrations of the reactants in the initial mixture are expressed in percentages by volume.

of the foil was kept constant to within 0.02 °C by means of a special thermoregulator. Above 180 °C, auto-oscillations in the rate of reaction were observed with a period ranging from 3 to 60 s. The reaction mixture contained a large excess of hydrogen and the oxygen concentration did not exceed 1 vol.%. With increase of temperature to 350 °C, an increase of the amplitude and frequency of the oscillations as well as an expansion of the range of pressures at which oscillations took place were observed. The maximum amplitude of the oscillations was 40% of the average rate of reaction. Simultaneously with the auto-oscillations in the rate of reaction, the authors[17] observed and investigated oscillations in the contact potential difference (CPD) for a nickel plate. Above 200 °C, oscillations were observed both in the reaction rate and in the CPD with a period ranging from 12 to 120 s. The amplitude and the frequency of the CPD oscillations were independent of the linear rate of flow of gases through the reactor.

Auto-oscillations in the reaction rate have also been found in the oxidation of hydrogen on platinum catalysts[18] (Fig. 1*e*). Owing to the difference between the types of influence of platinum and nickel catalysts on different reactants, the auto-oscillations in the rate on platinum catalysts were observed for other component ratios in the reaction mixture (in the presence of an excess of oxygen and small amounts of hydrogen). During the reaction on a platinum wire, auto-oscillations in the rate were observed at a catalyst temperature exceeding 135 °C for a reaction mixture containing 21.5% O_2 and >0.5% H_2. With increase of temperature from 160° to 200 °C, a decrease was observed in the amplitude and period of the auto-oscillations, the latter varying in the range from 220 to 6 s.

When hydrogen was oxidised on a platinum foil, oscillations in the CPD were noted simultaneously with oscillations in the reaction rate[18]. Auto-oscillations in the reaction rate were observed in the temperature range 85–130 °C for the same compositions of the reaction mixture as for the platinum wire. With increase of the hydrogen concentration in the reactor, the amplitude and period of the oscillations also increased, to maximum values, and then fell. When the temperature of the catalyst was varied in the range 85–130 °C, the period of the oscillations changed from 60 to 2 min.

Other workers[10,19] also observed auto-oscillations in the rate of oxidation of hydrogen on a catalyst grain containing 0.4% of platinum but under non-isothermal conditions. The period of the oscillations of the temperature of the centre of the platinum grain was 60 min and its amplitude was 60 °C. (about a mean value of 170 °C). The temperature of the gas stream, consisting of a mixture of air and 3.14% of hydrogen, was kept at 53 °C. The authors concluded that, despite the non-isothermal experimental conditions, the auto-oscillations are not associated with the characteristics of the interaction of the mass and heat transfer involving the catalyst grain. This conclusion was reached in the light of the long period of the oscillations and the absence of phase shift between the oscillations in the catalyst temperature and the concentration of the water formed.

The auto-oscillations in the rate of oxidation of ethylene by oxygen on a platinum wire have been studied[20] by the method of compensation electrothermography. The auto-oscillations in the rate were noted at a catalyst temperature exceeding 275 °C (Fig. 1*f*) in the presence of an excess of oxygen. The amplitude of the oscillations increased with increasing ethylene concentration and with decreasing catalyst temperature.

Auto-oscillations have been observed also in the rates of oxidation of cyclohexane on NaX, LiY, and KY zeolites[21,22] and of propene on the surfaces of CoO–MgO solid solutions[23]. The period of the auto-oscillations of the rate of oxidation of cyclohexane was ~0.5–10 min, the concentrations of the reactants and temperature varying periodically through the oscillations. Compounds of the peroxy-type were detected by infrared spectroscopy on the surface of the zeolite in the course of the reaction. The authors suggest that the oxidation of cyclohexane takes place by a heterogeneous-homogeneous mechanism.

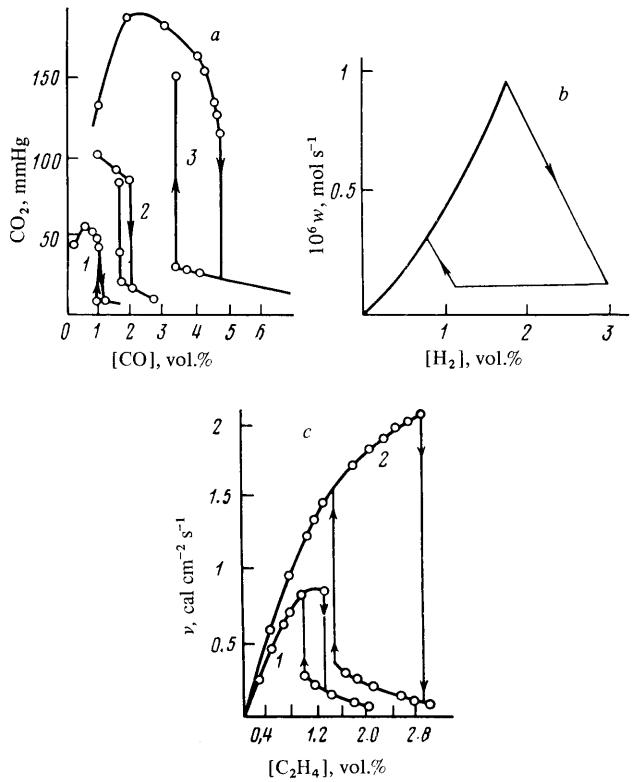


Figure 2. Dependence of the rate of reaction on the composition of the initial mixture for different heterogeneous catalytic systems: *a*) oxidation of CO on a deposited Pt catalyst[19] at different temperatures [temperature (°C): 1) 192; 2) 217; 3) 242]; *b*) oxidation of hydrogen on a platinum foil at 135 °C;[53] *c*) oxidation of ethylene on a platinum foil at different temperatures [temperature (°C): 1) 354; 2) 406].[20]

The data presented above show that auto-oscillations in the rate of reaction are observed in most cases in catalytic systems consisting of reactants differing sharply in their oxidation-reduction properties and containing a catalyst which is resistant to the formation of new bulk phases for a specified composition of the reaction mixture. For a number of heterogeneous catalytic systems, periodic conditions arise in the region of an uncertain dependence of the rate of reaction on the composition of the reaction mixture for a cyclic variation of the latter (i.e. in the region of hysteresis). Such phenomena have been observed in the oxidation of CO on platinum catalysts[9,10,19], in the oxidation of ethylene on a platinum wire[20], and in oxidation on a platinum

foil[53]. Fig.2 illustrates the dependence of the rates of the above reactions on the composition of the reaction mixtures; all the relations are similar. With increased concentration of a component which is present in the reaction mixture in a deficient amount, a gradual increase of the reaction rate is observed; above this the rate falls sharply. A decrease in the concentration of carbon monoxide, ethylene, or hydrogen leads to an increase of the rate of reaction, which, however, occurs at another (lower) concentration of the component present in a deficient amount.

Auto-oscillations in the rate have been observed either along the ascending branch or in the region of the maximum in the relation between the rate of reaction and the composition of the reaction mixture. Hysteresis has been observed[14] in the rate of oxidation of CO for a cyclic variation of the rate of flow of the reaction mixture through the reactor. The concentration of carbon monoxide at the inlet to the reactor was kept constant. Periodic changes in the rate of reaction have also been observed in the region of non-unique stationary states about an upper unstable stationary state.

Measurements of the contact potential difference in the course of the catalytic reaction have shown that the regions of maximum reaction rates and a multiplicity of stationary states are characterised by a high sensitivity of the activity of the catalyst to the composition of the gas phase and the surface layer. The marked influence of the composition of the adsorbed layer on the rate of the catalytic process is apparently one of the principal causes of the non-linear kinetic relations between the rate of reaction and the composition of the gas phase. Such complex relations, involving regions of non-unique stationary states, have been observed in reactions of carbon monoxide with hydrogen on a nickel catalyst[24] and in the oxidation of ammonia on platinum catalysts[25,26].

Fig.1 shows that the form of the oscillations observed in various reactions varies within wide limits from nearly harmonic to the form of relaxation oscillations (relaxation oscillations are characterised by an alternation of rapid and slow movements in the course of a single cycle). There is also a possibility of more complex oscillations. Fig.3*a* illustrates complex oscillations in the rate of oxidation of hydrogen on a platinum wire[53]. Fig.3*b* presents complex oscillations in the rate of heat evolution in the oxidation of ethylene on a platinum wire[20]. Complex irregular dynamic conditions in the oxidation of hydrogen on a platinum wire, illustrated in Fig.4, have also been observed[54]. Evidently oscillations with a small amplitude and a short period can be replaced by oscillations with larger values of these parameters (Fig.4*a*). After unequal time intervals, the oscillatory conditions can also be disturbed by a sharp decrease of the rate of reaction and can then return to the initial state (Fig.4*b*).

The auto-oscillations in the rates of heterogeneous catalytic reactions have been observed in reactors of different types on both deposited and metallic catalysts. In the study of the oxidation of CO on platinum catalysts this phenomenon was observed in flow reactors[10,12,13,19], in a gradient-free reactor

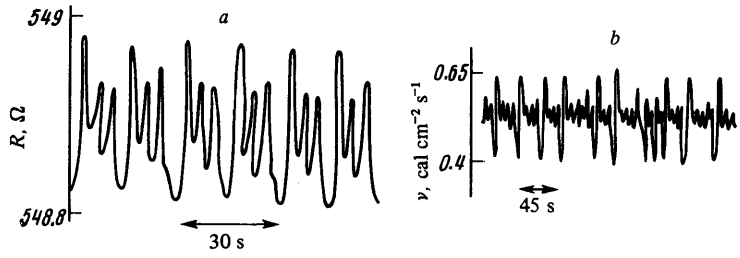


Figure 3. The form of the oscillations observed on platinum wire catalysts: *a*) variation of the resistance of the platinum wire *R* during the oxidation of hydrogen (2.8% H_2; 17.5% O_2; 79.7% N_2);[53] *b*) oscillations in the rate of heat evolution ν during the oxidation of ethylene (0.5% C_2H_4; 99.5% O_2).[20]

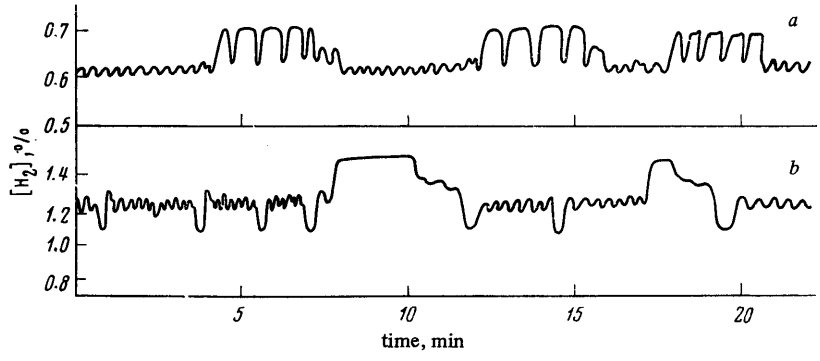


Figure 4. Complex oscillatory conditions observed on a platinum wire during the oxidation of hydrogen: *a*) 202 °C; 2.13% H_2, 21.5% O_2; *b*) 216 °C, 1.74% H_2, 15.6% O_2.[53]

with recycling[9], in a Carberry reactor[11], and in an ideal mixing reactor[14]. The auto-oscillations in the rates of oxidation of hydrogen on nickel and platinum catalysts[18], of ethylene on a platinum wire[20], and of cyclohexane on zeolite catalysts[21] have been studied in flow reactors.

In most cases auto-oscillations were detected under isothermal conditions or with a slight change in the catalyst temperature in the course of the oscillations. Thus, when CO was oxidised on a deposited catalyst, the temperature of the platinum grain changed by 2 °C [10,19] and in the study of the auto-oscillations in the rate of the same reaction on platinum catalysts in the form of a foil[14] and a wire[12] the change was by 3° and 5 °C respectively. Auto-oscillations in the rate of reaction of hydrogen with oxygen have been observed on a nickel foil whose temperature was kept constant in the course of the oscillations to within 0.02 °C.[16] This shows that the auto-oscillations in the rates of the above reactions are not associated with the influence of heat and material transport processes on the rate of reaction.

The nature of the observed auto-oscillations is determined by the catalyst temperature, the composition of the reaction mixture, and the composition of the catalyst surface. For all the oxidation reactions on metallic catalysts investigated, an increase of the rate of auto-oscillations with increasing temperature and the concentration of the component present in excess has been found. The frequency of the auto-oscillations depends much more on the concentration of the component present in the reaction mixture in a smaller amount. An increase of the period of the auto-oscillations in the rate of oxidation of carbon monoxide with increasing carbon monoxide concentration has been reported[11,14]. However, a decrease of the period of the auto-oscillations in the reaction rate for this process has been observed[9] with increase of the content of carbon monoxide in the initial mixture.

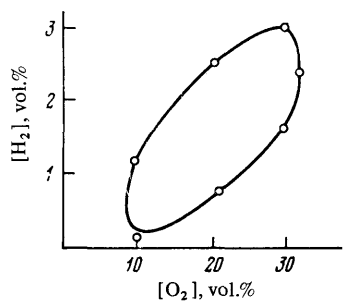


Figure 5. The region of the existence of auto-oscillations in the rate of oxidation of H_2 on a platinum foil in the plane corresponding to the variation of the hydrogen and oxygen concentrations at 85 °C.[18]

The variation of the period of the auto-oscillations in the rate of the hydrogen oxygen–reaction on a platinum foil with the initial concentration of hydrogen has a maximum whose height depends on the temperature[18]. With increase of the catalyst temperature, the amplitude of the auto-oscillations in the rate of reaction of hydrogen with oxygen on platinum catalysts fell. An analogous dependence of the amplitude of the oscillations in the rate on temperature has been noted in all studies of the reaction of carbon monoxide with oxygen.

On the other hand, on nickel catalysts an increase of the amplitude of the auto-oscillations in the rate of oxidation of hydrogen was observed with increase of temperature to 350 °C. The amplitude of the auto-oscillations depends also on the composition of the reaction mixture. With increase of the CO pressure, the amplitude of the auto-oscillations in the rate of oxidation of CO on a platinum catalyst increased. On nickel and platinum catalysts, a maximum has been observed in a number of experiments in the dependence of the amplitude of the auto-oscillation in the rate of oxidation of hydrogen on the composition of the reaction mixture. On a platinum foil, a closed region of auto-oscillations was found in the plane corresponding to changes in the concentrations of hydrogen and oxygen, illustrated in Fig.5.[18] The presence of critical concentrations of the reactants and a catalyst temperature for which auto-oscillations in the rate appear and vanish as well as the dependence of the amplitude and the frequency of the auto-oscillations on these parameters indicate the chemical nature of the observed phenomenon. A periodic variation of the contact potential difference, which was observed simultaneously with the auto-oscillations in the rate of reaction, indicates a change in the composition of the adsorbed layer. Fig.6 illustrates the auto-oscillations in the rate of reaction of hydrogen with oxygen on nickel (*a*) and platinum (*b*) catalysts measured simultaneously with the contact potential difference. Evidently the oscillations in the CPD have the same form and period as those in the rate of reaction. On a nickel catalyst, these quantities vary out of phase, while on a platinum foil there is no phase shift between the oscillations in the CPD and in the rate of reaction.

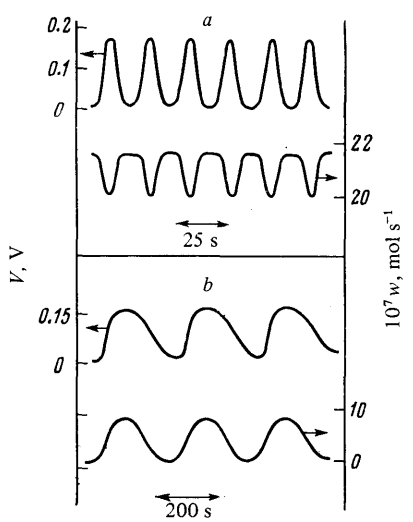


Figure 6. Auto-oscillations in the rate of oxidation of hydrogen on nickel (*a*) and platinum (*b*) catalysts recorded simultaneously with measurement of the changes in the CPD.[18]

Analysis of the CPD oscillations is difficult owing to the non-linear variation of the electron work function with the concentration of the adsorbed substances. However, it is known that the adsorption of oxygen on nickel and platinum leads to an increase of the electron work function and that this influence on the work function is stronger when the

influence of the hydrogen or carbon monoxide concentration is larger. Consequently, the form of the auto-oscillations in the rate of oxidation of hydrogen and in the CPD leads to the conclusion that an increase of the degree of surface coverage of nickel by oxygen and a decrease of the oxygen concentration on the platinum surface entail a decrease of the rate of reaction. The variation of the CPD between platinum and silicon with the ratio of carbon monoxide and oxygen in the reactor at different temperatures has been published[13]. It was shown that an increase of [CO] entails an increase of the CPD and a decrease of the rate of oxidation of CO. The form of the oscillations of the photocurrent, noted during this reaction on a platinum electrode, is analogous to the form of the oscillations of the CPD during the oxidation of hydrogen on a platinum foil. The rapid decrease in the amount of carbon monoxide or hydrogen on the surface, which leads to an increase of the rate of reaction, is replaced by a slower stage involving a return of the composition of the surface to the initial state.

III. PHYSICOCHEMICAL BASIS OF THE AUTO-OSCILLATIONS IN THE RATE OF REACTION

Auto-oscillating systems are well known in physics, engineering, and biology. Auto-oscillations are used particularly widely in radio-engineering, mechanics, and the control of technological processes. It is known from the theory of oscillations[2] that in most cases an auto-oscillating system should contain four fundamental elements: a constant (non-oscillating) source of energy or substance; an oscillating system, a device regulating the supply of energy or substance from the source to the oscillating system and feedback between the oscillating system and the regulating device (regulator), which acts by controlling the supply of the energy or substance. Auto-oscillating systems with a special feedback controlling the operation of a valve are called systems with an external feedback. External feedback can be absent and the valve can be controlled directly by the oscillating system. Such auto-oscillating systems are referred to as systems with internal feedback.

Auto-oscillating systems are divided into virtually harmonic systems and discontinuous or relaxation systems. The former have a high quality factor, a relatively small amount of energy is supplied during the period of the oscillation, and the energy in the oscillating system is exchanged between its elements. In systems of the second type dissipative forces play a significant role. In an oscillating system there exists one energy accumulator which either stores it or dissipates it. The period of the relaxation oscillations can frequently be divided into stages differing sharply in the rate of change of the state of the system. The boundary between the relaxation and harmonic auto-oscillations is not sharp and they can be regarded as a single physical phenomenon.

Auto-oscillatory conditions are impossible in linear systems and can arise only when there is a non-linearity in the system. In most cases the feedback is the source of the non-linearity. However, the presence of a feedback is not a sufficient condition for the occurrence of auto-oscillations; a definite force of this feedback is required.

In homogeneous chemical systems the feedback is determined by the auto-catalytic and inhibitory overall stages[5], as a result of which a closed sequence of stages appears in the system. Degn[6] indicated four possible types of feedback in homogeneous chemical systems. The presence of even one feedback in the system leads to the appearance of kinetic features different from the Law of Mass Action. However, Korzukhin[27] showed that, for any change in the concentrations of some of the reactants over a finite time interval, it is possible to construct a chemical system consisting of elementary stages whose rates are described by the Law of Mass Action.

The feedback in biochemical systems is in most cases achieved as a result of the influence of the substrate of the product on the activity of the enzyme and its properties[28].

Heterogeneous catalytic systems have many features in common with enzymatic systems. The reactants adsorbed on the catalyst surface can also exert a major influence on its catalytic properties. By considering the catalyst and the reaction medium as a single heterogeneous catalytic system, it can be shown that under certain conditions the heterogeneous catalytic system contains all the elements of an auto-oscillating system. The stationary flow of reactants entering the reactor in the direction of the catalyst surface constitutes a constant non-oscillating source of material. The oscillating system consists of a collection of adsorbed substances whose concentrations can vary periodically with time. By controlling the accumulation and consumption of the adsorbed substances as a result of adsorption and the reaction, the catalyst behaves as a regulator and the influence of the reactants on the properties of the catalyst can serve as the internal feedback from the system to the regulator.

In order to achieve non-decaying oscillations in the rate, it is necessary for accumulation to take place at each stage of the cycle, i.e. the rate of chemisorption of substances must exceed the rate of reaction, while in another stage the rate of reaction must be higher than the rate of accumulation. The catalyst as a regulator fulfills in this instant alternately the role of a source of negative and positive feedback. This is possible if the activity of the catalyst depends on the concentrations of the reactants on the catalyst surface. The application of the diffraction of slow electrons (LEED) in the study of catalytic systems made it possible to observe structural changes in the catalyst under the influence of the reactants in the course of adsorption and the reaction[29,30]. Such changes include a rearrangement and formation of new faces on the catalyst surface, the reconstruction of the surface with formation of mixed ordered surface layers containing the catalyst and reactant atoms, and the displacement of the positions of the atoms of the catalyst as a result of the formation of chemical bonds with the reactants. The formation of structures on the surface of platinum has been observed on different faces in the course of the adsorption of carbon monoxide[31] and hydrogen[32], while the adsorption of oxygen did not alter the surface structure of pure platinum up to complete saturation[31,33]. On the other hand, ordered surface structures were observed on nickel during the adsorption of oxygen[29,34,35] as a function of the face and the surface concentration, while hydrogen is capable of forming an ordered structure only on the (110) face of the nickel single crystal[36].

A period of increasing rate of reaction with decrease of the surface coverage by oxygen has been observed on the (110) and (100) faces of a nickel single crystal[37]. The authors[37] suggest that the development of the reaction requires the generation of "islands" of the pure nickel phase and that the rate of reaction is determined by the length of the boundary between these islands. An analogous topochemical type of reaction has been proposed[38] to account for the interaction of hydrogen with oxygen preadsorbed on the (110) nickel face and in another study[39] for the oxidation of hydrogen on a platinum catalyst.

The change in the properties of the catalyst as a result of adsorption in the reaction can be explained within the framework of the electron gas theory developed by Temkin[40]. According to this theory, the energetic properties of the surface are determined by the number of electrons in the surface layer of the catalyst and hence by a number of atoms adsorbed on the catalyst surface which supply and remove these electrons. A change in the amount of adsorbed substance entails a linear change in the activation energies for the adsorption process and the reaction on the catalyst surface. When substances with different donor–acceptor properties are adsorbed, the properties of the electron gas change, and this is reflected in the influence of the adsorption of one substance on that of the other. Thus the adsorption of carbon monoxide can alter the reaction properties of the hydrogen adsorbed on platinum[41]. In its presence a change in the rate of adsorption of oxygen on a platinum catalyst was also observed[31]. The influence of oxygen on the strength of the bond formed by hydrogen and carbon monoxide with the platinum surface has been observed[42]. With increase of the surface coverage by adsorbed oxygen, an increase of the amount of hydrogen or carbon monoxide, adsorbed in a state with much higher bond energies than on a clean surface, has been noted.

IV. MATHEMATICAL MODELS

The modelling of auto-oscillating systems is based mathematically on the general theory of oscillations, according to which auto-oscillations arise in non-linear systems with feedback. In order to elucidate the mechanism of the influence of feedback in heterogeneous catalysis, it is necessary to have an idea about the changes in the concentrations of the reactants on the catalyst surface during the reaction. In the studies discussed above such measurements could not be made and the construction of a detailed mathematical model is therefore difficult. One of the first mechanisms suggested for the operation of feedback in heterogeneous catalytic systems was one where the reactants influence the activity and properties of the catalyst[16]. The possibility of this mechanism of feedback is indicated by experimental data for the adsorption and reactions of a number of substances on metallic catalysts, which were described in the previous section. This type of feedback has been used[18] to construct a mathematical model of the reaction of hydrogen and oxygen on nickel and platinum catalysts.

The mathematical model of the oxidation of hydrogen on an element of the catalyst surface must reproduce the principal features of the process: the adsorption of hydrogen and oxygen and the interaction of the adsorbed substances, without specifying further the details of the mechanism:

$$\begin{gathered} O_2 + 2[M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2[M{-}O], \\ H_2 + 2[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2[M{-}H], \\ [M{-}O] + 2[M{-}H] \xrightarrow{k_3} 3[M] + H_2O. \end{gathered} \tag{1}$$

where [M] is a free site on the catalyst surface, [M–O] and [M–H] represent the oxygen and hydrogen adsorbed on the free catalyst site, and k_i ($i = \pm 1$, ± 2, or ± 3) are the rate constants for the corresponding reaction stages.

Experimental studies of this reaction showed that there is only a slight dependence of the characteristics of the auto-oscillations on the rate of flow of the reactants through the reactor. Oscillations in the CPD have been observed for a relatively small change in the composition in the gas phase. Consequently one may claim that the auto-oscillations in the rate of reaction are due to periodic processes on the catalyst surface. This made it possible to treat the hydrogen and oxygen pressures as constant and to assume that they are equal to the average values for the period.

The kinetic model describing the changes in the surface concentrations of adsorbed oxygen (θ_O) and hydrogen (θ_H) is of the following type:

$$\begin{aligned} \frac{d\theta_O}{dt} &= k_1 p_{O_2} (1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_3\theta_O\theta_H^2 = Q(\theta_O, \theta_H), \\ \frac{d\theta_H}{dt} &= k_2 p_{H_2} (1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_3\theta_O\theta_H^2 = P(\theta_O, \theta_H), \end{aligned} \tag{2}$$

where p_{O_2} and p_{H_2} are the oxygen and hydrogen pressures in the gas phase.

Eqns.(2) do not entail limiting cycles in the phase plane, since the Bendickson criterion holds for it: if the expression $\partial P/\partial x + \partial Q/\partial y$ has a constant sign in a single-phase region of the phase plane, then there are no closed contours in this region. It is readily seen that throughout the θ_O and θ_H phase plane the expression $\partial Q(\theta_O, \theta_H)/\partial P(\theta_O, \theta_H)/\partial\theta_H$ is always negative. In this case there is a unique stable stationary state of the type of a node or focus in system (2) for all values of the parameters. Auto-oscillations of the rate are impossible in the system, since one of the fundamental elements of an auto-oscillating system, namely the feedback, is absent.

The feedback arising from the influence of the reactants on the activity and properties of the catalyst can be expressed by the dependence of the activation energy for the adsorption and reaction stages on the hydrogen and oxygen concentrations on the catalyst surface. We shall analyse the simplest case where the concentrations of the adsorbed substances influence only the rate of the surface interaction of the reactants, the activation energy for this stage varying linearly with the degree of surface coverage by oxygen and hydrogen in accordance with the equation

$$E_3 = E_{30} + \alpha_1\theta_O + \alpha_2\theta_H. \tag{3}$$

The rate constant for the third stage can then be formulated as follows:

$$k_3 = k_{30}\, e^{(\mu_1\theta_O + \mu_2\theta_H)},$$

where the parameters $\mu_1 = \alpha_1/RT$ and $\mu_2 = \alpha_2/RT$ can be both greater and smaller than zero.

The variation of the rate of oxidation of hydrogen on nickel catalysts under the conditions of an excess of hydrogen and low oxygen concentrations in the gas phase can be due to the variation of the amount of adsorbed oxygen[37]. If the rate constant for the third stage varies with the degree of surface coverage by oxygen in accordance with the expression

$$k_3 = k_{30}\, e^{-\mu_1\theta_O}, \tag{4}$$

where $\mu_1 > 0$ and $\mu_2 = 0$, then, when account is taken of Eqn.(4), Eqns.(2) can be written as follows:

$$\begin{aligned} \frac{d\theta_O}{dt} &= k_1 p_{O_2} (1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2\, e^{-\mu_1\theta_O} = Q(\theta_O, \theta_H), \\ \frac{d\theta_H}{dt} &= k_2 p_{H_2} (1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2\, e^{-\mu_1\theta_O} = P(\theta_O, \theta_H). \end{aligned} \tag{5}$$

Here the functions $Q(\theta_O, \theta_H)$ and $P(\theta_O, \theta_H)$ have been determined in the region $G = \{(\theta_O, \theta_H): \theta_O + \theta_H \leq 1;\ \theta_O \geq 0;\ \theta_H \geq 0\}$ and all the $k_i > 0$ ($i = \pm 1$, ± 2, or ± 3).

Eqns.(5) have been studied[55] by the phase plane method. Relations were found between the parameters for which a single unstable stationary state surrounded by stable limiting cycle is possible in the system. The following theorem was used to find periodic solutions of Eqns.(5).

Suppose that C is a cycle without contact and F is the region bounded by it. There exists at least one stable cycle if the following conditions are fulfilled: (1) all the trajectories intersecting C with increasing t enter F; (2) in the region F there is a single unstable stationary state of the type of a node or focus.

Linearisation of Eqns.(5) in the vicinity of the stationary state with θ_O^s and θ_H^s leads to algebraic expressions of the following type:

$$\frac{d\theta_O}{dt} = a_{11}(\theta_O - \theta_O^s) + a_{12}(\theta_H - \theta_H^s),$$
$$\frac{d\theta_H}{dt} = a_{21}(\theta_O - \theta_O^s) + a_{22}(\theta_H - \theta_H^s),$$

where

$$a_{11} = \left(\frac{\partial Q}{\partial \theta_O}\right)_{\theta_O^s, \theta_H^s}, \quad a_{12} = \left(\frac{\partial Q}{\partial \theta_H}\right)_{\theta_O^s, \theta_H^s},$$
$$a_{21} = \left(\frac{\partial P}{\partial \theta_O}\right)_{\theta_O^s, \theta_H^s}, \quad a_{22} = \left(\frac{\partial P}{\partial \theta_H}\right)_{\theta_O^s, \theta_H^s}$$

The stability of the stationary state is determined by the roots of the following characteristic equation:

$$\lambda^2 - (a_{11}+a_{22})\lambda + (a_{11}a_{22} - a_{12}a_{21}) = \lambda^2 - \sigma\lambda + \Delta = 0 . \quad (6)$$

A sufficient condition for the existence of a unique stationary state throughout the region of the parameters is

$$\frac{dQ(\theta_O, \theta_H)}{d\theta_O} < 0. \quad (7)$$

When the above condition holds, the following inequality is always valid: $\Delta(\theta_O, \theta_H) > 0$ along the curve

$$P(\theta_O, \theta_H) = 0 \quad (8)$$

Denoting the transport of oxygen to the surface by $k_1 p_{O_2}(1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 = G_O$ and the rate of reaction by $k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O^2} = w$, condition (8) can be formulated thus:

$$\frac{dG_O}{d\theta_O} < \frac{dw}{d\theta_O}. \quad (9)$$

The physical significance of condition (9) is that in the stationary state the variation of the rate of reaction with oxygen concentration on the surface should be greater than the variation of the rate of transport of the latter to its surface. Condition (9) is valid when the following inequality holds:

$$2k_{-1} > k_{-2}(\mu_1 - 1). \quad (10)$$

In order that limiting cycles should arise in the system defined by Eqns.(5), the condition $\sigma(\theta_O^s, \theta_H^s) > 0$ must be fulfilled together with condition (10). This is achieved for $\mu_1 > 30$. The high values of μ_1 for which auto-oscillations in the rate of reaction arise in system (5) show that there must be a strong influence by the adsorbed substances on the properties of the catalyst.

System (2) has also been studied in the presence of various functional types of influence of the concentrations of the reactants on the properties of the catalyst. The form of the feedback was specified by the function $f_i(\theta_O)$ in the expression for the change in the rate constant for the third stage as a function of the degree of surface coverage by oxygen:

$$k_3 = k_{30} f_i(\theta_O).$$

For auto-oscillations to arise in system (2) with $f_1(\theta_O) = (1 - \theta_O)^{\mu_1}$ it is necessary that $\mu_1 > 20$, and for a feedback of the type $f_2(\theta_O) = (1 + \theta_O)^{-\mu_1}$, it is necessary that $\mu_1 > 37$.

A detailed study of a system of type (2) with the above types of feedback has been carried out in a general form for a system taking into account the different orders of the adsorption and desorption reactions of the reactants and its results can be used to find the conditions for the occurrence of auto-oscillations in kinetic models of both the hydrogen oxidation reaction on nickel and platinum catalysts and the carbon monoxide oxidation reaction on platinum catalysts.

The mathematical model of an auto-oscillating heterogeneous reaction of type (5) has many features in common with the system of differential equation describing the behaviour of a non-isothermal ideal mixing reactor[43]. The identical structure of the differential equations entails the similarity of the dynamic behaviour of the processes in the ideal mixing reactor and on a surface element of the catalyst. A detailed study of the properties of an ideal mixing flow reactor[44] revealed a multiplicity of phase plots observed in this system. The decisive parameters are the kinetic criterion and the adiabatic heating criterion, the Damköhler number, and the rate of removal of heat by the cooling unit. Depending on the values of these parameters, nine types of phase plots are possible, on five of which stable limiting cycles are possible. The cause of the auto-oscillations is the presence of a feedback via the influence of the temperature of the reaction mixture on the rate of reaction. This influence of the temperature is analogous to auto-catalysis. With increase of temperature, there is a sharp increase of the rate of reaction relative to the rate of supply of the reactants, which entails a decrease of the concentrations of the reactants in the reactor and a lowering of the temperature, which in its turn gives rise to a sharp fall of the rate of reaction relative to the rate of supply of the reactants. On subsequent increase of the amount of reactants in the reactor up to the critical concentration, a sharp increase of the rate begins again.

Condition (11), the fulfillment of which over the entire range of parameters guarantees a unique stationary state, is well known for thermokinetic oscillations:

$$\frac{dG_T}{dT} > \frac{dw}{dT}, \quad (11)$$

where G_T is the transport of heat to the reactor and w the rate of reaction. Conditions (9) and (11) are analogous in form and differ only by their signs due to the different influences of the adsorbed substances and temperature on the rate of reaction.

In an adiabatic ideal mixing reactor auto-oscillations of the rate of reaction are impossible. Additional removal of heat by the cooling unit is necessary for auto-oscillations to occur. Similarly additional removal of oxygen from the surface of the catalyst by desorption is essential for the auto-oscillations of the rate of reaction of hydrogen with oxygen on a nickel catalyst.

Sets of parameters for which limiting cycles arise have been found for system (5).[55] One of these limiting cycles, which exist about an unstable stationary state, is illustrated in Fig.7.

In conformity with the nature of the change in the degree of surface coverage by hydrogen and oxygen, it is possible to visualise the following mechanism of the generation of auto-oscillations. With increase in the amount of adsorbed oxygen on the surface of the nickel catalyst, the rate of reaction falls and the surface is covered by oxygen and hydrogen. Next, in consequence of the desorption of oxygen, there is a rapid decrease of its concentration on the catalyst surface. After

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#See E.A.Ivanov, G.A.Chumakov, M.G.Slinko, D.D.Bruns, and D.Luss, Chem.Eng.Sci. (in the Press).

the attainment of the limiting value of θ_O, the quantity $e^{-\mu_1\theta_O}$ begins to increase rapidly as θ_O diminishes, the adsorbed hydrogen and oxygen react at a high rate, and the surface is almost completely freed from oxygen. Then the adsorption of oxygen begins again and leads to an increase of its concentration on the catalyst surface and the inhibition of the reaction. This process terminates the cycle. The above mechanism of the auto-oscillations of the rate of reaction is analogous to the mechanism of the thermokinetic auto-oscillations in an ideal mixing reactor with the difference that the reactants are supplied by chemisorption and the acceleration of the reaction is determined by the influence of the amount of adsorbed oxygen on the rate of formation of water.

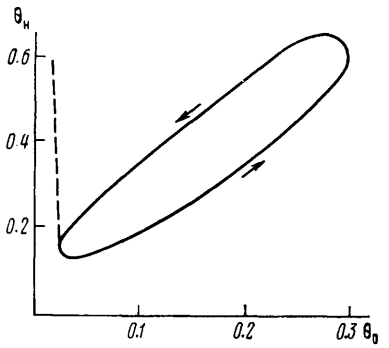


Figure 7. The limiting cycle of model (5) found for the following system parameters: $k_1 p_{O_2} = 15.6\ s^{-1}$; $k_{-1} = 1\ s^{-1}$; $k_2 p_{H_2} = 30\ s^{-1}$; $k_{-2} = 0$; $k_3 = 10^{-5}\ s^{-1}$; $\mu_1 = 40$.[55]

The auto-oscillations of the rate observed in the oxidation of hydrogen on platinum have also been described in terms of feedback of type (3).[53] However, in view of the different composition of the reaction mixture and the decrease of the stationary rate of reaction with increasing hydrogen pressure in the gas phase, the influence of the hydrogen concentration alone on the activation energy for the stage involving the interaction of the adsorbed substances was examined and α_1 was assumed to be zero. On the assumption that $\mu_2 = \alpha_2/RT$, the dependence of the rate constant for the third stage on the surface coverage by hydrogen can be written in a form analogous to Eqn.(4):

$$k_3 = k_{30}\, e^{-\mu_2\theta_H}. \qquad (12)$$

Taking into account Eqn.(12), Eqns.(2) can be written as follows:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2 e^{-\mu_2\theta_H}$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_2\theta_H} \qquad (13)$$

The mechanism of the development of auto-oscillations in this system is analogous to that presented above for system (5).

Models (5) and (13) were compared with experimental data obtained for the interaction of hydrogen with oxygen on nickel and platinum catalysts respectively. These models reflect correctly the nature of the change in the amplitude and the critical conditions for the appearance and disappearance of auto-oscillations as the composition of the reaction mixture is varied. However, the models are of limited validity for the description of low-frequency oscillations. When the calculated and experimental rates averaged over the period of oscillations agreed, the maximum period of the auto-oscillations calculated on the basis of models (5) and (13) was ~1 s. Such frequencies were observed on a nickel foil and a platinum wire at high temperatures. At lower temperatures, low-frequency oscillations were noted, which cannot be described in terms of models (5) and (13). The maximum periods in models (5) and (13) are reached when k_{-1} and k_{-2} respectively are reduced. When these constants approach zero, the auto-oscillations in the rate of reaction vanish. This indicates the necessity for the existence of an additional removal of the substance influencing the catalytic activity of the metal from the surface of the catalyst.

Bearing in mind the low rates of desorption of oxygen from platinum[45] and nickel[46] catalysts, Zelenyak and Slin'ko[56] added to mechanism (1) a stage involving the Eley–Rideal impact mechanism, during which the adsorbed oxygen can be removed from the surface and can react with the gas-phase hydrogen:

$$[M - O] + H_2 \xrightarrow{k_4} [M] + H_2O. \qquad (14)$$

Allowance for this stage leads to the appearance of an additional term in the mathematical model (5), describing the removal of oxygen from the surface of nickel. The dynamic behaviour of the new system is unaltered if the rate constant for the fourth stage is independent of the degree of surface coverage by adsorbed substances. It is natural to suppose that the adsorbed oxygen decreases the rates of all the water formation stages in the oxidation of hydrogen on a nickel catalyst. Assuming that the activation energy for the fourth stage E_4 increases linearly with the degree of surface coverage by oxygen, i.e. $E_4 = E_{40} + \alpha_4\theta_O$, we obtain a mathematical model in the following form:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1 - \theta_O - \theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2 e^{-\mu_2\theta_O} - k_{40} p_{H_2}\theta_O e^{-\mu_4\theta_O},$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1 - \theta_O - \theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_2\theta_O}. \qquad (15)$$

With the aid of model (15), it is possible to obtain a much better agreement between the experimental and calculated data. Auto-oscillations at low frequencies for a high average rate during the period arise if the following relation between the constants holds:

$$k_1 p_{O_2},\ k_{40} \gg k_2 p_{H_2},\ k_{-2},\ k_{30}.$$

In this case the slow variation of the degree of surface coverage by hydrogen ensures a low oscillation frequency, while a high rate of reaction is attained as a result of the high rate of the impact stage.

A qualitative study of system (15) has been carried out by Belyaev, Chumakov, and Plikhta§. They showed that the introduction of an additional parameter, in relation to system (5), complicates the dynamic behaviour of the system. Fig.8 illustrates the types of phase plots which are possible in the given system. Evidently, depending on the values of the parameters, up to five stationary states and stable and unstable limiting cycles can arise in the system.

The dynamic behaviour of the hydrogen and carbon monoxide oxidation reactions is surprisingly similar. Attention was drawn to this by Langmuir as early as 1918 [47] and was confirmed by the experimental investigations of Kuchaev and Temkin[45,48], who observed that the kinetics of these two

§Quoted by T.I.Zelenyak and M.G.Slin'ko, Kinetika i Kataliz, 18, 1235 (1977).

reactions have many features in common and can be described in terms of analogous mechanisms, including both impact and adsorption reaction pathways. The following mechanism has been proposed[48] for the oxidation of CO:

$$\begin{gathered} O_2 + 2\,[M] \overset{k_1}{\rightarrow} 2\,[M{-}O] \\ CO + [M] \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [M{-}CO] \\ [M{-}O] + [M{-}CO] \overset{k_2}{\rightarrow} 2\,[M] + CO_2 \\ [M{-}O] + CO \overset{k_4}{\rightarrow} [M] + CO_2 \end{gathered} \qquad (16)$$

The kinetic model corresponding to mechanism (16) has a form analogous to that of system (2) and differs from it only by the different orders of the adsorption and desorption reactions of one of the components of the reaction mixture and also by the additional term describing the interaction of the adsorbed oxygen with gaseous carbon monoxide:

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_{CO})^2 - k_{-1}\theta_O^2 - k_3\theta_O\theta_{CO} - k_4 p_{CO}\theta_O, \\ \frac{d\theta_{CO}}{dt} = k_2 p_{CO} (1 - \theta_O - \theta_{CO}) - k_{-2}\theta_{CO} - k_3\theta_O\theta_{CO} \end{gathered} \qquad (17)$$

The difference between the orders of adsorption and desorption reactions of the reactants is responsible for the possible appearance in system (17) of several stationary states, since condition (8) can break down. However, the Bendickson criterion remains negative over the entire range of parameters and auto-oscillations are therefore impossible. In order to explain the appearance of auto-oscillations, one must take into account, by analogy with the preceding systems, the experimental decrease of the rate of reaction with increasing CO pressure in the gas phase. One can then postulate the following dependence of the activation energies for the third and fourth stages on the degree of surface coverage of the catalyst by carbon monoxide:

$$\begin{aligned} E_3 &= E_{30} + \alpha_1\theta_{CO}, \\ E_4 &= E_{40} + \alpha_2\theta_{CO}. \end{aligned} \qquad (18)$$

Taking into account the influence of adsorbed carbon monoxide on the rate constants for the third and fourth stages, we obtain a kinetic model for the oxidation of carbon monoxide analogous to Eqns.(15):

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_{CO})^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_{CO}\, e^{-\mu_1\theta_{CO}} - k_{40} p_{CO}\theta_O\, e^{-\mu_2\theta_{CO}}, \\ \frac{d\theta_{CO}}{dt} = k_2 p_{CO} (1 - \theta_O - \theta_{CO}) - k_{-2}\theta_{CO} - k_{30}\theta_O\theta_{CO} e^{-\mu_1\theta_{CO}}. \end{gathered} \qquad (19)$$

This system can be used to compare the calculated and experimental parameters of the oscillations in the oxidation of CO on platinum.

Mechanism (16) and feedback of type (3) have also been used[14] to construct a kinetic model of the auto-oscillations of the rate of oxidation of CO on platinum catalysts. The authors examined four types of models consisting of two differential equations and differing in the choice of dynamic variables. Mathematical analysis of the model including the oxygen and carbon monoxide pressures in the gas phase as dynamic variables showed that auto-oscillations in the rate of reaction are possible only for unrealistic values of the parameters of the model. Oscillatory conditions were observed in models where the pressure of carbon monoxide in the gas phase was chosen as one of the dynamic variables while the degrees of surface coverage either by oxygen or by carbon monoxide or by one of the forms of adsorbed carbon monoxide served as the second dynamic variable. For this choice of dynamic variables, the surface concentration of the second reactant was assumed to correspond to equilibrium with respect to its pressure in the gas phase. The authors[14] in no way justified the choice of the dynamic variables of the models. It remains obscure why only one of the surface concentrations is stationary with respect to the gas phase. The experimental CPD and the photocurrent during the auto-oscillations of the rate of reaction show that a more probable cause of the development of auto-oscillations in the rate of reaction is oscillations in the composition of the surface of the catalyst,

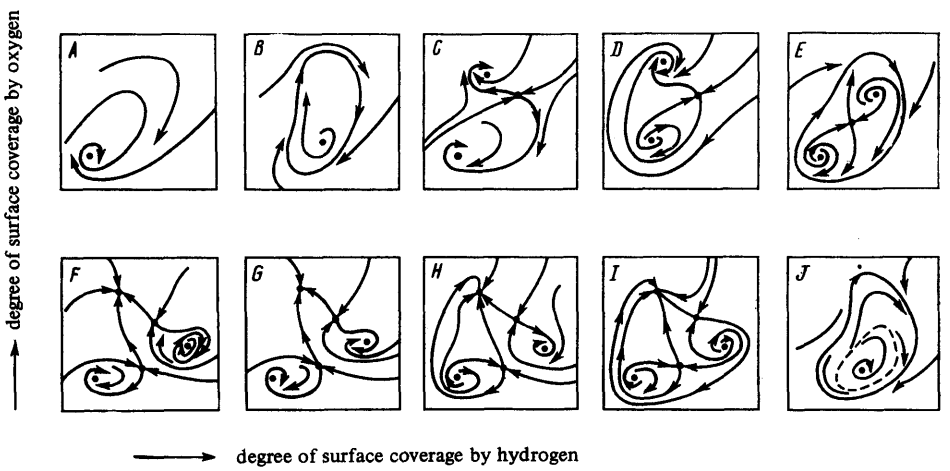


Figure 8. Phase plots for system (15) obtained for different values of the parameters of the model[56].

which can be non-stationary in relation to the composition of the gas phase.

The data obtained in the study of the auto-oscillations of the rates of heterogeneous catalytic reactions show that the periods of the auto-oscillations vary within wide limits—from 1 to 3600 s. The lower limit of this range is determined by the inertia and the upper limit by the stability of the instruments with the aid of which auto-oscillatory conditions are detected. The occurrence of auto-oscillations with long periods necessitates the assumption of the existence of phenomena which decrease the frequencies of the auto-oscillations. One of such causes may be the presence on the surface of an inactive form of the reactant, which constitutes a kind of buffer of the active form on the surface and can reduce the frequency of the auto-oscillations. It is known[49] that two forms of adsorbed hydrogen can exist on platinum catalysts. Presumably the adsorption of hydrogen on the surface of the platinum catalyst takes place with formation of an inactive form H_i. The latter can then be converted on the surface into the active form H_a, which interacts with the adsorbed oxygen. The reaction mechanism is formulated as follows:

$$\begin{gathered} O_2 + 2\,[M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,[M{-}O]\ , \\ H_2 + 2\,[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\,[M{-}H_i]\ , \\ [M{-}H_i] \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} [M{-}H_a]\ , \\ 2\,[M{-}H_a] + [M{-}O] \xrightarrow{k_3} 3\,[M] + H_2O\ . \end{gathered} \tag{20}$$

If the active hydrogen on the surface alters the rate constant for the third stage in accordance with the expression

$$k_3 = k_{30}\, e^{-\mu_3 \theta_{H_a}},$$

then the kinetic model can be formulated as follows in conformity with mechanism (20):

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - \theta_{H_a} - \theta_{H_H})^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}, \\ \frac{d\theta_{H_H}}{dt} = k_2 p_{H_2} (1 - \theta_O - \theta_{H_a} - \theta_{H_H})^2 - k_{-2}\theta_{H_H}^2 - k_H\theta_{H_H} + k_{-H}\theta_{H_a}, \\ \frac{d\theta_{H_a}}{dt} = k_H\theta_{H_H} - k_{-H}\theta_{H_a} - 2k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}. \end{gathered} \tag{21}$$

If k_i, $k_{-i} \gg k_1$, k_{-1}, k_2, k_{-2}, k_3, then the active and inactive forms of hydrogen are in equilibrium and there is a linear relation between their surface concentrations:

$$\theta_{H_i} = K_p \theta_{H_a}, \tag{22}$$

where $K_p = k_{-i}/k_i$.

Taking into account Eqn.(22), it is possible to formulate a system of differential equations [Eqns.(23)] describing the variation of the concentration of surface oxygen and the overall concentration of the hydrogen adsorbed in two forms:

$$\begin{gathered} \frac{d\theta_O}{dt} = k_1 p_{O_2} (1 - \theta_O - (1 + K_p)\,\theta_{H_a})^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}, \\ (1 + K_p)\frac{d\theta_{H_a}}{dt} = k_2 p_{H_2} (1 - \theta_O - (1 + K_p)\,\theta_{H_a})^2 - k_{-2}K_p^2\theta_{H_a}^2 - \\ - 2k_{30}\theta_O\theta_{H_a}^2 e^{-\mu_3\theta_{H_a}}. \end{gathered} \tag{23}$$

In Eqns.(23) there is an additional term on the left-hand side of the differential equation, compared with system (13), representing the inertia $(1 + K_p)$. The appearance of this term increases the period of the oscillations for values of the parameters close to those for system (13). Thus, when the amount of the active form of hydrogen is twice that of the inactive form ($K_p = 0.5$), the period of the auto-oscillations increases by a factor of two.

A possible mechanism of the development of auto-oscillations with participation of the active and inactive forms of one of the reactants was also examined by Eigenberger[50]. Assuming the existence of two forms of oxygen adsorbed on platinum, the author proposed the following mechanism for the oxidation of carbon monoxide on platinum catalysts:

$$\begin{gathered} CO + [M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [M{-}CO]\ , \\ O_2 + 2\,[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\,[M{-}O_a]\ , \\ 2\,[M{-}O_a] + 2\,[M{-}CO] \xrightarrow{k_3} 2CO_2 + 4\,[M]\ , \\ O_2 + 2\,[M] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} [M{-}O_{2i}]\ . \end{gathered} \tag{24}$$

Next he assumes that the amount of oxygen adsorbed in an active form is in equilibrium with respect to its pressure in the gas phase and is small owing to the high rate of desorption ($k_{-2} \gg k_2 p_{O_2}$). With these postulates, mechanism (24) assumes the following form:

$$\begin{gathered} CO + [M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [M{-}CO]\ , \\ 2\,[M{-}CO] + O_2 + 2\,[M] \xrightarrow{k_3} 2CO_2 + 4\,]M]\ , \\ O_2 + 2\,[M] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} [M{-}O_{2i}]\ . \end{gathered} \tag{25}$$

The feedback in this sytem also occurs via the influence of the adsorbed substances on the rate of formation of carbon dioxide. However, it is assumed that this influence is not exerted by the adsorbed substances on the catalytic properties but occurs via the change in the number of active sections of the catalyst surface involved in the reaction. This form of feedback can occur subject to the author's assumption[50] that the concentration of the active form of oxygen is low owing to the high rate of its desorption from the surface of platinum. Despite the fact that this conflicts with experimental data showing low rates of desorption of oxygen from platinum, the author[50] was able to account for the region of development and the periods of the auto-oscillations in the rate of oxidation of CO on a platinum mesh observed by Hugo and Jakubith[9].

The buffer capacity for the adsorbed substance active in the reaction can be created not only on the catalyst surface as a result of substances inactive in the reaction but also in the surface layer of the catalyst due to the dissolved reactants. The high solubility of hydrogen in nickel[51] can lead to the saturation of the surface layer of the latter by hydrogen when the reaction takes place in an excess of this gas. If the rate of dissolution of hydrogen is assumed to be proportional to the rate of coverage of the catalyst by hydrogen and to the fraction of vacancies in the metal accessible to dissolved hydrogen while the rate of diffusion of hydrogen from the metal is assumed to be proportional to the amount of dissolved hydrogen and the fraction of surface free from adsorbed hydrogen, then the change in the fraction of hydrogen dissolved in nickel will be described by the following equation[55]:

$$\frac{dz_H}{dt} = K_5\theta_H (1 - z_H) - K_{-5} z_H (1 - \theta_H), \tag{26}$$

where $K_5 = k_5 NS/V$, $K_{-5} = k_{-5} NS/V$, z_H is the concentration of hydrogen dissolved in the surface layer of the catalyst and referred to the limiting concentration of the dissolved hydrogen, N the number of adsorbed atoms per cm^2 of the catalyst, S the catalyst area, and V the volume of the surface layer of the catalyst.

If $K_5 = K_{-5} = K \gg k_1$, k_{-1}, k_2, k_{-2}, k_3, then the fraction of hydrogen dissolved in the metal will be proportional to its surface concentration: $z_H = K\theta_H$.

If Eqn.(26) is added to mechanism (1), then system (5) can be formulated as follows:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O},$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O} - \frac{dz_H}{dt}. \quad (27)$$

Since $dz_H/dt = Kd\theta_H/dt$, we obtain system (28), which differs from system (5) only by the inertia term. It appears in the equation describing the variation of the fraction of the surface covered by hydrogen:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H)^2 - k_{-1}\theta_O^2 - k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O},$$
$$(1+K)\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_1\theta_O}. \quad (28)$$

With increase of K, there is an increase in the amount of dissolved hydrogen in equilibrium with adsorbed hydrogen, which increases the period of the auto-oscillations.

In the general case both components of the gas phase can dissolve in the surface layer of the metal and the overall mechanism of the interaction of hydrogen and oxygen includes the following stages in this case:

$$O_2 + 2[M] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2[M{-}O],$$
$$H_2 + 2[M] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2[M{-}H],$$
$$2[M{-}H] + [M{-}O] \xrightarrow{k_3} 3[M] + H_2O,$$
$$[M{-}O] + H_2 \xrightarrow{k_4} [M] + H_2O,$$
$$[M{-}H] + [M_V] \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} [M_V{-}H] + [M],$$
$$[M{-}O] + [M_V] \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} [M_V{-}O] + [M],$$

where $[M_V]$ is an atom in the surface layer of the metallic catalyst and $[M_V{-}H]$ and $[M_V{-}O]$ are the hydrogen and oxygen atoms dissolved in the surface layer.

Assuming that in a thin surface layer of the catalyst there is virtually complete mixing, one can formulate a generalised kinetic model as follows:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H)^n - k_{-1}\theta_O^p - k_4 p_{H_2}\theta_O - k_3\theta_O\theta_H^2 - \beta_O\frac{dz_O}{dt},$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^m - k_{-2}\theta_H^q - 2k_3\theta_O\theta_H^2 - \beta_H\frac{dz_H}{dt}, \quad (29)$$
$$\frac{dz_H}{dt} = k_5\theta_H(1-z_H) - k_{-5}z_H(1-\theta_H-\theta_O),$$
$$\frac{dz_O}{dt} = k_6\theta_O(1-z_O) - k_{-6}z_O(1-\theta_H-\theta_O),$$

where n, m, p, and q are the orders of the corresponding stages and β_O and β_H are the limiting amounts of oxygen and hydrogen dissolved in the surface layer of the catalyst and expressed in terms of the number of monolayers.

In the interpretation of the experimental data obtained in the study of the oxidation of hydrogen on platinum catalysts the following additional assumptions were made[57]: (1) the adsorption and desorption of hydrogen are second-order reactions, while the adsorption and desorption of oxygen are first-order reactions: $m=q=2$ and $n=p=1$; (2) the concentration of oxygen in the surface layer of the platinum catalyst changes little: $dz_0/dt \cong 0$; (3) the hydrogen dissolved in a thin surface layer of platinum increases linearly the activation energy for the water formation stages:

$$E_3 = E_{30} + \gamma_3 z_H,$$
$$E_4 = E_{40} + \gamma_4 z_H.$$

These assumptions lead to the following relations between the rate constants for the water formation stages and the amount of dissolved hydrogen:

$$k_3 = k_{30}e^{-\mu_1 z_H};\ k_4 = k_{40}e^{-\mu_2 z_H},$$

where $\mu_1 = \gamma_3/RT$ and $\mu_2 = \gamma_4/RT$. With these assumptions, the form of the kinetic model (29) is:

$$\frac{d\theta_O}{dt} = k_1 p_{O_2}(1-\theta_O-\theta_H) - k_{-1}\theta_O - k_{40}p_{H_2}\theta_O e^{-\mu_2 z_H} - k_{30}\theta_O\theta_H^2 e^{-\mu_1 z_H},$$
$$\frac{d\theta_H}{dt} = k_2 p_{H_2}(1-\theta_O-\theta_H)^2 - k_{-2}\theta_H^2 - 2k_{30}\theta_O\theta_H^2 e^{-\mu_1 z_H} - \beta_H\frac{dz_H}{dt}, \quad (30)$$
$$\frac{dz_H}{dt} = k_5\theta_H(1-z_H) - k_{-5}z_H(1-\theta_H-\theta_O).$$

Depending on the values of the parameters, system (30) makes it possible to describe both relaxation auto-oscillations and auto-oscillations which are nearly harmonic over a wide range of frequencies. The form of the auto-oscillations is determined by the relative values of the group of rate constants $k_1 p_{O_2}$, $k_2 p_{H_2}$, k_4, k_3, and k_{-2} for the processes occurring on the surface and the constants k_5 and k_{-5} characterising the involvement of the surface layer in the reaction. The period of the auto-oscillations depends on the rate of exchange between the surface and the bulk of the layer.

A novel mathematical model, also consisting of three differential equations, has been proposed[52] for the interpretation of the experimental auto-oscillations in the rate of oxidation of CO on platinum catalysts[12,13]. The authors[52] based their model on mechanism (16). In order to account for the development of auto-oscillations in the rate of reaction, they assumed a temperature difference between the first active layers of the catalyst and the external medium, whose temperature was assumed to be equal to that of the deep layers of the catalyst. It was also assumed that the rates of all the stages vary exponentially with the temperature of the surface layer of the catalyst. The mechanism of the development of auto-oscillations reduces in this case to the following: in the first instant the interaction of the adsorbed reactants proceeds at a low rate and the sites on the catalyst surface liberated by the reaction are immediately occupied by oxygen. The heat evolved in the reaction accelerates the surface interaction of carbon monoxide with oxygen and this autocatalytic process terminates only when the entire surface of the metal has been covered by oxygen. After this, the surface is rapidly cooled and the removal of oxygen from it begins as a result of its interaction with the carbon monoxide in the gas phase; this reaction takes place at a virtually constant temperature of the surface layer. As soon as the concentration of oxygen on the surface has been reduced and that of carbon monoxide increased, the surface interaction of these substances begins and leads to a new rise in the temperature of the surface layer and the cycle is repeated.

The above mechanism shows that the feedback arises in this case owing to the influence of the temperature of the surface layer on the rate of reaction. The mathematical model has a form analogous to that of model (30), but the third equation describes the change in the temperature of the surface layer of the catalyst and not the change in the concentration of hydrogen dissolved in the surface layer. Analysis of the mathematical model showed that the mechanism of the auto-oscillations in the rate described above is possible for long thermal relaxation times. Estimates of thermal relaxation times in the course of reactions on metals lead to much smaller values, so that the model described by the authors[52] is physically unsound.

V. CONCLUSION

The data presented above show that in recent years there has been a sharp increase of the number of studies and publications devoted to the auto-oscillations in the rates of heterogeneous catalytic reactions. This is because the discovery of this phenomenon is important for the development of the theory of the kinetics of heterogeneous catalytic reactions. The auto-oscillations in the rate observed in heterogeneous catalysis show that the catalytic properties of the surface vary under the influence of the catalytic process and that the composition of the surface can be non-stationary in relation to the composition of the gas phase. The auto-oscillations in the rate of reaction occur only under conditions remote from equilibrium. From this it follows that the mechanisms of heterogeneous catalytic reactions can be different in the vicinity of and far from equilibrium conditions. The reaction on different active sections of the catalyst surface remote from one another takes place synchronously.

The amplitude and period of the auto-oscillations in the rate of reaction are very sensitive to the structure of the catalytic system and to the values of its parameters. There is a possibility of quasi-harmonic, relaxation, complex, and random oscillatory conditions. The frequencies of the auto-oscillations vary within wide limits. The development of oscillations with low frequencies indicates the occurrence in the system of stages which are slower than that involving the formation of the final products.

The mathematical models of the auto-oscillations in the rates of heterogeneous catalytic reactions consist of systems of two or several non-linear differential equations. Their form and properties depend on the way which the results of the catalytic process influence its characteristics. This feedback can be due to various causes, namely: (a) the change in the reaction rate constant under the influence of the change in the concentrations of the reactants on the surface or in a thin surface layer of the catalyst; (b) competition by stages involving the adsorption of the reactants and a change in the number of active sites on the catalyst surface during the reaction; (c) superheating of a thin layer of the catalyst surface; (d) the development of homogeneous-heterogeneous stages in the catalytic process; (e) a complex sequence of three and more surface stages.

The present scope of experimental studies in the field of catalysis is limited owing to the lack of methods for the continuous observation of the composition and temperature of the surface and of the surface layer of the catalyst. At the present stage of investigations the choice of a particular type of feedback and a complete quantitative description of the auto-oscillations in the rates of heterogeneous catalytic reactions are therefore difficult. In order to develop a theory of the auto-oscillations, it is also necessary to establish a relation between the reaction at the molecular level and the observed rate and to elucidate the causes of the synchronisation of the oscillations on individual active sites of the surface. Thus one may hope that studies in the field of the auto-oscillations in the rate will permit a more complete investigation of the kinetics and will lead to the elucidation of the mechanisms of heterogeneous catalytic reactions.

During the preparation of the review for the press, studies on auto-oscillatory conditions have been combined into a new field of the kinetics of heterogeneous catalytic reactions. The first investigations of the auto-oscillations in the rates of heterogeneous catalytic reactions were part of the programme of an international congress devoted to the kinetics of physicochemical oscillations, which was held on 19th September 1979 in Aachen (German Federal Republic). During this period, there has been a significant increase of the number of heterogeneous catalytic systems in which the given phenomenon has been observed. These include the interaction of NO and CO on polycrystalline platinum[58], the oxidation of methanol on aluminosilicate catalysts containing palladium[59], the oxidation of ammonia on platinum–rhodium catalysts[60], and the oxidation of octane, hexane, and 1-propanol on platinum catalysts in the presence of organophosphorus compounds[61]. The oscillations in the rate of reaction of NO and CO are interesting because they arise at a pressure of only 5×10^{-4} mmHg, while the auto-oscillations in the rate in all other known systems have been observed only at atmospheric pressure.

Further investigation of the auto-oscillations in the rate of oxidation of CO on deposited and metallic platinum catalysts revealed a high sensitivity of the region where the oscillations occur and of their properties to the composition of the reaction mixture. It has been found that the addition of but-1-ene[62] and of organophosphorus compounds[61] to the initial reaction mixture induces the appearance of auto-oscillations in the rate of the reaction. It has been shown[63] that when electrolytic oxygen is used in the oxidation of carbon monoxide on deposited platinum catalysts, auto-oscillations arise in the rate of reaction whose properties are different from those of the oscillations in the rate of reaction involving oxygen obtained from air and containing a significantly larger amount of impurities. Modelling of the auto-oscillations in the rate of reaction in the given system has been continued[64,65]. The most complete interpretation of the experimental data published previously[9] has been achieved by Ali and Hugo[65]. The authors used model (17), having taken into account the activation energies for the third and fourth stages of mechanism (16) in the adsorption of both components of the reaction mixture. The model also takes into account the influence of the adsorbed oxygen on the activation energy for the CO desorption stage and the influence of both adsorbed components on the activation energy for the oxygen adsorption stage.

The study of the auto-oscillations in the rate of oxidation of hydrogen on platinum[66] and nickel[67] catalysts has also been continued. Particular attention has been devoted to the investigation of complex and irregular dynamic conditions, which have recently been referred to as random oscillations. Thorough experimental proof that the existence of random oscillations in the oxidation of hydrogen on a nickel foil has been published[67]. A mechanism has been proposed[68] for this reaction whose kinetic model can reflect the observed[67] random oscillations in the rate of reaction. The interest in complex and random oscillations can be explained by the fact that they can arise only in systems described by three and more differential equations. This imposes additional limitations on the possible reaction mechanism. Thus the reaction mechanism proposed by Schmiltz et al.[68] includes stages involving the alternate oxidation and reduction of the surface. It is suggested that the reduced surface is inactive, while the adsorption of the reactants and the reaction between them take place only on the oxidised surface. The mathematical model of the reaction also includes an equation describing the variation of the temperature of the catalyst surface. Random oscillations have been observed[66] in the rate of oxidation of H_2 on a platinum wire. The authors[66] believe that the random oscillations can be induced by the incomplete synchronisation of the rates of reaction on different catalyst surface sites.

A homogeneous-heterogeneous mechanism of the oxidation of cyclohexane on the NaX zeolite has been examined by Berman and Elinek[69]. They proposed a non-stationary kinetic model, which describes the variation of the gas-phase concentrations of the peroxy-compounds and peroxy-radicals

formed in the oxidation of cyclohexane. The model describes the earlier results qualitatively[22].

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