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Review

Molar heats of chemisorption of gases at metals: Review of experimental results and technical problems

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ABSTRACT

Technical and procedural problems in measurements of the heats of chemisorption (CHS), including the urgency of generalization of the technical and procedural problems and the ways of their solution, specificity of calorimetric studies of CHS, design of the glass calorimetric ampoules and vacuum apparatuses for studies of CHS at powders, and approaches to extraction of information on the mechanisms of CHS and catalytic processes from CHS and calorimetric studies, are considered. The importance of data on the heats of CHS for solution of the "homogeneity" vs. "heterogeneity" problem is substantiated. The available results of adsorption and calorimetric studies of CHS at industrial catalysts approached to their states occurring under conditions of catalytic processes, the effect of improvement of the techniques and procedures, and numerous results of studies of the molar heats of CHS of CO, H_2, O_2, N_2, and hydrocarbons at metals and some oxides for about 60 gas–chemadsorbent systems are collected and discussed. It is concluded that surfaces reveal themselves as homogeneous.

Contents

1. Technical and procedural problems in measurements of the heats of chemisorption

1.1. Specificity of calorimetric studies of chemisorption as compared with calorimetric studies of other chemical processes

Correct measuring of the heats of chemisorption (CHS) or desorption of small portions of gases is a rather complicated problem,

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and the quality of its solution depends not only on the skill of experts in calorimetry but also on the current state of the adsorption techniques and procedures. The matter is that the heat effects in CHS experiments are rather small and are usually equal to no more than 0.1–0.4 J. Meanwhile, they should be measured correctly, should be cleaned from the heat effects of side processes and should be related to the amounts of chemadsorbates that are just chemisorbed but not participate in other physicochemical processes. The requirements to the quality of the measurements of the heats of CHS are very high, because a solution of the problem of "heterogeneity" vs. "homogeneity" of surfaces of catalysts and chemadsorbents, which is of fundamental importance for the theories of catalysis, CHS, and solids, depends on the results of these measurements. This problem relates just to the thermally stabilized surfaces of solids that function as catalysts or chemadsorbents and are subjected to the action of a reacting gaseous (or liquid) reacting mixture under conditions of stationary catalytic processes or CHS equilibriums. It is important for the theories of CHS and catalysis and for their practical applications, because the formulation of science-based methods and procedures intended for modeling of industrial catalytic and CHS technologies and reactors depends on the solution of this problem. It is also important for the solid-state theory in the context of the question: is the reactive ability of a solid-body surface controlled by the characteristics of its individual atoms or by the characteristics of the surface as a whole?

Among the processes that can accompany CHS are interaction of chemadsorbates with substances chemisorbed previously and formation of surface or gaseous products; interaction of chemisorbed grease vapors with chemadsorbates; chemadsorbate diffusion into solid bodies; interaction of chemadsorbates with impurities or with solid components diffusing from the body to the surface; chemadsorbate adsorption on walls of adsorption apparatuses; chemical interaction between chemadsorbates and walls of adsorption apparatuses, metal taps, and balances; sintering of samples during calorimetric experiments; chemical interaction of grease vapors with chemadsorbents or (and) chemadsorbates, and so on. In the course of CHS experiments, each of these processes can influence the values of the heat effects, gas amounts actually chemisorbed or desorbed, chemadsorbate surface/body distribution, specific surface area, or adsorption characteristics of the samples. Some of these side processes can affect two or more these parameters simultaneously. All side phenomena should be precluded or taken into consideration, and the experiments should be performed under the conditions minimizing them.

For calorimetric and kinetic studies of CHS of a gas at an adsorbent, the choice of correct combinations of the initial chemadsorbate pressure, pressure range for measuring of the CHS rates, size of the chemadsorbent grains, and thickness of the chemadsorbent layer are of great importance. The matter is that the integral heat effects give no information on the mechanism of processes. Therefore, the researchers orient themselves on studies of the coverage dependences of the rates and molar heats of CHS. Meanwhile, the equal availability of the entire porous surface area for chemadsorbates is necessary to obtain correct dependences of these parameters on the degree of coverage. Specific demands should be made to the microcalorimeters intended for CHS studies and to the adsorption apparatus—calorimeter interfaces. Some peculiarities of the calorimeters that are currently in use for calorimetric studies of CHS at vacuum-evaporated films and single crystals and at powders are considered in [1] and in [2–5], respectively. Most of the measurements of the heats of CHS of gases at powders were performed with differential double isoperibol calorimeters supplied with the Tian's thermostat and with thermocouple batteries (Calvet's calorimeters [2]) or Pt-thermoresistors (FOSKA calorimeters [3,5]) as the sensitive elements. The theories of measurements with Calvet's calorimeters and with FOSKA calorimeters are detailed in the classical monograph [2] and in [3,5], respectively.

Some special features and technical and procedural approaches, consideration of which is desirable when differential double calorimeters are used for studies of the molar heats of CHS of gases and vapors at metals and oxides, are described below.

1.2. Calorimetric ampoules

First, we describe those special features and technical and procedural approaches that relate to the sample, calibrating, and comparative calorimetric ampoules and to the point of junction of the adsorption apparatus with the sample and comparative (or sample and calibrating) calorimetric ampoules.

(1) CHS calorimetric experiments have features that distinguish them from many other calorimetric experiments. First, on frequent occasions, each CHS experiment starts at a pressure at which the gas flow into the sample ampoule is viscous (the so-called Poiseuille flow) and terminates at almost full vacuum, i.e., the final portion of the experiment proceeds under the conditions when the gas flow into the sample ampoule is molecular (the so-called Knudsen flow). Second, the heat effects under consideration are influenced by the difference between the temperature of a calorimetric ampoule and of a gas incoming to it. Third, the heat effects measured in the experiments, in which chemadsorbates are dosed portion-by-portion, are influenced by the heat of gas throttling through the tap opening.

During the experiments, the heat flows that are directed from calorimetric ampoules to the outside in vertical direction and that are unidentifiable by the heat-flow sensors are pressure-independent (or almost independent) and pressure-proportional in the beginnings and in the endings of the experiments, respectively; over an intermediate pressure region, the thermal conductivity is pressure-dependent, although it is not proportional to the pressure. If the sample and comparative (or calibrating) ampoules are not connected to each other, this peculiarity leads to the pressure dependence of the calorimetric sensitivity, because the heat-effect portion fixed by the sensors of the heat flow varies in the course of any one experiment.

In CHS experiments, the initial pressure over chemadsorbent is usually about 0.1 hPa and decreases as CHS proceeds; the diameter of the tube that joins a calorimetric ampoule with a vacuum apparatus and through which a heat leaves the calorimeter, omitting the heat sensors, is usually about 5 mm. At 0.1 hPa and 298 K, the mean free path of H_2 and O_2 molecules is equal to 1.48 and 0.85 mm, respectively, and increases with temperature. We see that the mean free path and the diameter of the heat-conducting tube are of the same order of magnitude and, therefore, the calorimetric sensitivity should be pressure-dependent. Meanwhile, each one calorimetric experiment proceeds over a wide range of the pressure, and ignoring of the effect under consideration inevitably should lead to erroneous results. It was experimentally shown that this effect is significant up to a pressure of about 0.65 hPa [6]. For example, the sensitivity in vacuum was 17.21 μV/mW, 37% lower than that under atmospheric pressure of air and the sensitivity increased from about 17 μV/mW under vacuum to about 22 μV/mW under 0.13 hPa of He. We see that the effect is rather significant. Note that the importance of the effect under consideration for studies of physical adsorption, which are usually carried out at high pressures, is much less significant, because the pressure dependence of the thermal conductivity of gases at pressures exceeding several hectopascals is small.

In [5,7], we described the means and procedures allowing for eliminating this effect, which is extremely harmful for CHS studies. However, the effect under consideration has been ignored up to now in a number of works. It is quite necessary to take efficient actions aimed at full identity of the sample, calibrating, and comparative ampoules in their sizes and heat capacity and in geometries of their internal contents and to introduce gas portions into two ampoules simultaneously. Therewith, the calibrating-resistance coil in the calibrating ampoule, inert material (e.g., small glass bits or spheres) in the comparative ampoule, and the adsorbent in the sample ampoule should have equal heat capacities and masses (see [5]). Under such conditions, the advantages of the differential method of the heat measurements can be used completely; namely, the effect of the change in the gas-flow character can be automatically taken into account by the differential electrical circuit in the course of adsorption experiments. It is clear that two identical parasitic heat effects will affect oppositely the differential electric signal, and, thus, the heat effect under study will be measured correctly. The identity of calorimetric ampoules in combination with the symmetric joining of the sample and calibrating (or comparative) ampoules to the line leading to the vacuum apparatus allows the automatic consideration of two other parasitic heat effects that are capable to affect the heat effects under study. The first one is the difference in the temperatures of the calorimetric ampoules and of the gas incoming to them. The second one is the heat effect of the gas throttling through the tap opening. A portion of the throttling heat evolves in calorimetric ampoules and influences the heat effect under measurement. The symmetric joining of two identical ampoules to the gas line provides automatic subtraction of this parasitic heat effect and promotes measuring of the actual heats of CHS.

The fulfillment of the recommendations considered in this item makes calorimetric studies of CHS significantly more precise.

(2) The maximum height of the chemadsorbent layer in the sample ampoule (along with the maximum height of the heat-emitting element in the calibrating ampoule and the maximum height of the layer of the inert material in the comparative ampoule) should be chosen in such a way that neither some its decreasing nor some its increasing could influence coverage dependence of the molar heat (the fulfillment of this recommendation in any study should be stated experimentally). Otherwise the results of calibrating may be inapplicable for calculation of the heat effects of CHS.

This recommendation is caused by a limitation of the range of the heat-emitting-layer heights for which the heat-flow portion directed upward from a calorimetric ampoule and unidentifiable by the heat-flow sensors is independent of the layer height (see [8]).

(3) The most reliable results can be obtained when chemadsorbent grains are rather small, the layer thickness is 1–2 grains, and the initial pressure in each experiment corresponds to the conditions when the free path of the molecules of chemadsorbate is no less than the diameter of the most abandon pores of the chemadsorbent. Fulfillment of these conditions is very desirable in order that the entire chemadsorbent, including its porous structure, be equally accessible to the gas molecules in the course of each experiment. When the chemadsorbent-layer thickness is great and the initial pressure in CHS experiments is high, the layer-by-layer CHS can proceed, likely to gas adsorption in the gas-defense boxes of respirators, and, on frequent occasions, the coverage dependences of the molar heats and rates of CHS can not be revealed. The phenomenon of the layer-by-layer adsorption is well known after the studies that were performed in the early 20th century and were aimed at the development of scientific grounds for poison-gas protection; however, not all researchers take this phenomenon under consideration, and such works in which the adsorbent layers are of many centimeters in height are available.

(4) The heat running away from the calibrating ampoule through the electric wires should be taken into account in the course of calibration [5].

1.3. Glass vacuum apparatuses for calorimetric studies of chemisorption at powders

Below, we consider the recommendations that can be given as applied to the glass vacuum apparatuses (below, apparatuses) intended for obtaining reliable and rather exact data on CHS at powders (we do not consider trivial requirements, such as necessity of rather accurate measuring of the internal volumes of apparatuses, gas pressures, and so on).

(1) Any contact of chemadsorbents with vapors of hydrocarbon greases should be excluded, or it should be reliably proved that the vapors of the applied grease by no means adsorb at the adsorbent and interact with it and with the substances adsorbed or chemisorbed at it.

The matter is that the samples housed into calorimetric adsorption ampoules joined to adsorption apparatuses containing greased taps can physically adsorb the grease vapors at room temperature at nights or during holidays if a tap greased with the hydrocarbon grease is located between the ampoule and the apparatus. The trap located between the adsorbent and the tap and cooled during experiments to 77 K does not preclude such a possibility because, during nights or holidays, it can be heated up to room temperature and the grease vapors can contact with the adsorbent. If the adsorbent contains oxygen (chemisorbed at the metal or belonging to the oxide), the adsorbed grease can be oxidized up to chemisorbed water and carbon dioxide. The corresponding stoichiometric equations are given below.

$$\mathrm{MeO} + \mathrm{C}_n\mathrm{H}_{2n+2} = \mathrm{MeO}[\mathrm{C}_n\mathrm{H}_{2n+2}]_{\mathrm{ads}} \tag{1}$$

$$\begin{aligned}&\mathrm{MeO}[\mathrm{C}_n\mathrm{H}_{2n+2}]_{\mathrm{ads}} + 4n\,\mathrm{MeO}\\ &\quad = (4n+1)\,\mathrm{Me}\,n\,[\mathrm{CO}_3]_{\mathrm{ads}} + (n+1)[\mathrm{H}_2\mathrm{O}]_{\mathrm{ads}}\end{aligned} \tag{2}$$

Before the subsequent experiments, when the adsorbent is heated up to the experimental temperature and the trap is cooled to 77 K, CO_2 and H_2O desorb completely or partially and condense in the cooled trap according to the reaction

$$\begin{aligned}&(4n+1)\,\mathrm{Me}\,n\,[\mathrm{CO}_3]_{\mathrm{ads}} + (n+1)\,[\mathrm{H}_2\mathrm{O}]_{\mathrm{ads}}\\ &\quad = (3n+1)\,\mathrm{Me} + n\,\mathrm{CO}_2 + (n+1)\,\mathrm{H}_2\mathrm{O} + n\,\mathrm{Me}\end{aligned} \tag{3}$$

As a result, the adsorbent state changes and becomes indefinite, because some amount of oxygen desorbs from the chemadsorbent in the composition of H_2O and CO_2. Incompleteness of CO_2 and H_2O desorption creates an additional problem. During subsequent CHS experiments, some amounts of CO_2 and H_2O desorb with negative heat effects and condense in the cooled trap; desorption of these substances creates an indeterminateness in the heat of CHS of the chemadsorbate under study.

Therefore, the use of hydrocarbon greases is undesirable and makes sense only under condition of application of special reliable techniques and procedures for quantitative analysis of CO_2 and H_2O (such methods are described in [7]). Meanwhile, up to the 1960s, the researchers of CHS at powders everywhere applied such greases, and this is one of the important causes of unreliability of the CHS data obtained at that time.

The use of hydrocarbon greases led to erroneous values of the heats of CHS and to curious artifacts (see [7]). For example, it was published [9] that CHS of tens of O_2 monolayers at gold foil was observed. The ampoule with the Au chemadsorbent was protected from the greased tap by a trap cooled to 77 K. During a day, the gold foil was being covered by oxygen. During the following night, the trap was heated from 77 K to room temperature and the grease vapors physadsorbed at the foil and steadily converted at its surface by chemisorbed oxygen to chemisorbed water and chemisorbed carbon dioxide. The next day, after the trap was cooled again to 77 K, the ampoule with the foil was heated to the temperature of the experiments, and oxygen portions were dozed into the volume with the foil, oxygen chemisorbed at Au and H_2O and CO_2 desorbed from the foil and condensed in the trap. These procedures were continued for several days, and, day after day, hydrocarbons oxidized chemisorbed oxygen. These alternating processes produced an illusion that oxygen chemisorption corresponded to the capacity of many monolayers.

The effect of grease on the heat of oxygen CHS at silver will be demonstrated below. A sample of silver powder was reduced by hydrogen at an elevated temperature, degassed, and cooled to room temperature, at which it stayed for the weekend. For this time, it adsorbed grease vapors, and, when oxygen was admitted to the sample, the heat of grease oxidation to CO_2 and H_2O was measured instead of the heat of O_2 CHS.

Currently, silicon greases are widely distributed (hydrocarbon greases are also in use), because the vapor pressure over them is lower than that over hydrocarbon greases. No negative effects of silicon greases on the results of CHS measurements are described in the literature. However, no experimental proofs for their harmlessness in CHS studies are available.

(2) CHS apparatuses should provide rather accurate measurements of CO_2 and H_2O (and other gases) that can desorb from the samples under study. The greases are not the only source of CO_2 and H_2O in the apparatuses intended for CHS studies. If the powdered chemadsorbents are prepared on the basis of carbonates, the residual CO_2 and H_2O can diffuse to the surfaces of the samples and desorb during CHS and calorimetric measurements (if the samples are prepared on the basis of nitrates, H_2O and NO_x can desorb). The preliminary thermo-vacuum treatment of powders prepared on the basis of carbonates is usually incapable of full cleaning of CO_2 and H_2O from the samples.

Lack of evidence for the absence of CO_2 and H_2O desorption in the course of experiments on CHS of any gas can induce doubts in the accuracy of the measurements. If CO_2 and (or) H_2O desorb, corresponding corrections for the heats of their desorption are necessary. The means allowing for accurate analyzing CO_2 and H_2O vapors are also necessary to study quantitatively H_2 or CO CHS at oxides or at metals covered with oxygen, O_2 CHS at reduced metals (that can contain sorbed hydrogen), alternating H_2, CO, and O_2 CHS at metals or oxides, and CHS of gases and vapors in other systems at ideal chemadsobents completely free of the residual CO_2 and H_2O that could be absorbed in the course of preparation of the chemadsorbents.

Therefore, the data on the heats of CHS measured in glass vacuum apparatuses containing no sufficiently sensitive means for CO_2 and H_2O analyzing can be perceived as doubtful. No correct interpretation of the chemisorbed amounts and the heats of CHS is possible until methods of controlling of H_2O and CO_2 desorption are created and applied.

Simple and reliable arrangement allowing for quantitative analyzing of 1–50 mm^3 of CO_2/H_2O vapor mixtures with a sensitivity of 0.1 μmol is described in detail in [7] (this arrangement was also applied to analyze the $CH_3OH/HCOH/HCOOH$ [10], $NH_3/H_2/N_2$ [10,11], and some other mixtures).

(3) Adsorption at internal walls of the adsorption apparatus should be minimized. As was shown above, CHS of different gases at powders is on frequent occasions accompanied by side desorption of CO_2 and H_2O from samples. Therefore, measurements of the molar heats of CO_2 and H_2O CHS are necessary to introduce corrections into the heat effects measured during CHS of the chemadsorbates under study. Adsorption of CO_2 and H_2O at glass tubes and other articles of apparatuses hampers correct measurements of the molar heats of CO_2 and H_2O CHS. To preclude adsorption at the glass surfaces, a heating of the glass up to 400–410 K and any other technical approaches are very desirable. Such heating can be realized on the basis of using an outer wire electric heater [7]; in review [7], some other approaches are also described.

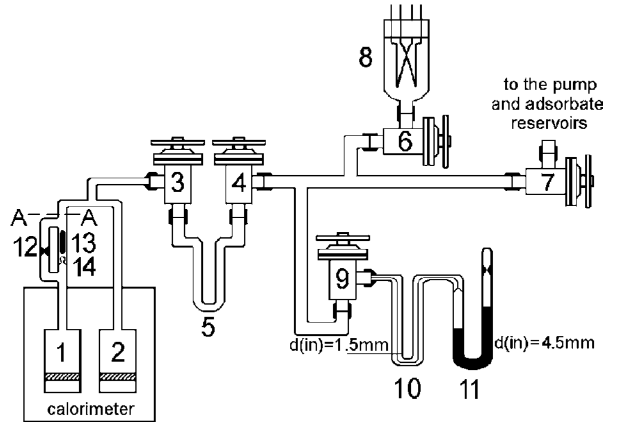

Fig. 1. Principal fragment of an improved glass apparatus intended for studies of chemisorption and desorption, including the heat effects of these processes, at powders: 1, sample ampoule; 2, reference ampoule; 3, 4, 6, 7, 9, metal bellows taps; 5, glass trap; 8, thermocouple manometer; 9–10–11, device for analyses (10, capillary trap; 11, mercury manometer); 12, neck; 13, magnetic cylinder; 14, diaphragm.

Fig. 1 presents an example of a vacuum apparatus answering the above recommendations. The detailed description of the apparatus and experimental procedures are given in [7,12].

1.4. Two principal approaches to extraction of information on the mechanisms of chemisorption and catalytic processes from chemisorption and calorimetric studies

Apparently, two principal purposeful approaches are possible: obtaining of information which is strictly in point to a real catalytic process or of information which is strictly in point to a CHS process and is indirectly in point to one or several catalytic processes. Among the studies of the first group are, for example, the studies aimed at revealing the mechanisms of the CH_3OH synthesis from H_2 and carbon oxides [10] and of the NH_3 synthesis from N_2 and H_2 [11,13] at $ZnO/Cu_4(OH_2)/Al_2O_3$ and $Fe/K_2O/Al_2O_3$ catalysts, respectively. To the second group, numerous studies of chemisorption of individual gases at films, wires, powders, and supported powders relate.

In the course of the studies relevant to the former and to the latter of these groups, some common and some specific technical and procedural problems should be solved.

One of the common problems that should be solved in any calorimetric study of CHS at adsorbents used in any aggregate state (powders, films, filaments, wires, etc.) is prevention of sintering during CHS and calorimetric measurements. If this problem is not solved, the heat of sintering can uncontrolledly contribute to the heat effects measured in the experiments and the surface area can decrease uncontrolledly during them. To prevent sintering, the samples should be preliminary treated at temperatures significantly higher than those of the subsequent calorimetric studies of CHS. Naturally, no contact of the samples with the atmosphere between preliminary treatment and experiments should occur.

The principal difference between the preliminary treatments of the samples intended for the studies of the former and latter groups lies in the following.

For the studies of the former group, the samples should be preliminary reduced rather well, the surfaces and the bodies of the reduced samples should be cleaned of the biographic H_2O,

CO_2, and other impurities capable of vaporizing in the course of the thermo-vacuum treatment and should be saturated with controlled amounts of all components of a real reaction mixture occurring in the catalytic process under study. Calorimetric experiments on CHS and desorption of each of the components should be performed with the samples obtained as a result of such a treatment. The point is that, in the course of any stationary catalytic process, the catalyst surface and body are in equilibrium (or almost-equilibrium) with the gas mixture and only one rate-determining reaction step prevents equilibrium. Therefore, to clarify the reaction mechanism on the basis of CHS and calorimetric data, the states of chemisorbents should be approached to those corresponding to the conditions of the real catalysis. Such a pretreatment is rather laborious and requires a rather long time for its performance. Therefore, the studies of the former group are rather rare. The difficulties are caused by the necessity of creation of the initial state of the samples under vacuum conditions, by the necessity of quantitative analyzing of two or three gaseous substances in the experiments on CHS or desorption of one of them, and by the necessity of consideration of the corresponding heat effects of CHS of each of them in each of the experiments (CHS of any one substance at the samples thus pretreated can lead to desorption of one or two other prechemisorbed substances). In reward for the efforts, such studies are capable of giving direct information on the composition of the surface layer, molar heats of CHS of chemadsorbates, degree of the surface homogeneity, and reaction ability of the chemisorbed components at the surface-layer states approached to those occurring in the course of real catalytic processes. All such information taken together can give a unique set of data on the mechanism of a catalytic reaction under study. As examples, we can make references to [10,11] relating to the syntheses of CH_3OH and NH_3.

As for the studies of the latter group, the samples should be reduced, the surfaces and the bodies of the reduced samples should be cleaned of the biographic vaporizable impurities, including H_2O and CO_2, and, after that, the samples thus obtained are ready for CHS and calorimetric experiments. Of course, such studies (as the studies of the former group) can be used for conclusions on the degree of homogeneity of chemisorbents only under the condition that the adsorption apparatuses allow for quantitative controlling CO_2 and (or) H_2O desorption during CHS experiments or if the experimental conditions are chosen in such a way that diffusion of these substances to the surface and their desorption are certainly impossible.

The features mentioned in the last paragraph are of great importance also for the quantitative fixation of the states of complete reduction and complete degassing of the samples before experiments. Meanwhile, in a number of adsorption and calorimetric works, the apparatuses have no means allowing for fixation of such states or available means are insufficiently sensitive.

During CHS experiments, a portion of chemisorbed gas can absorb into the sample body with a molar heat effect differing from the heat effect of CHS. It is commonly known that a number of metals of VIII group, revealing themselves as catalysts (Pd, Pt, Ir, Rh, Ni, and so on), are capable of absorbing H_2 to different extents; we will show below that, even under low pressures, iron and lanthanides are capable of absorbing H_2 and copper is capable of absorbing O_2. The molar heats of absorption of gases by metals are usually lower than the molar heats of CHS, and the grater is the surface coverage by a chemadsorbate, the higher is the rate of chemadsorbate diffusion into the solid body. Therefore, absorption is capable of falsifying coverage dependences of the heats of CHS and of creating false conclusions on decreases in the molar heats of CHS with surface coverages. To obtain information on CHS, it is necessary either to prove that absorption does not proceed, or to preclude it, or to take it into consideration. No data on a decrease in the heats of CHS with the surface coverage can be accepted if the possibility of absorption is not discussed.

This review is dedicated to CHS at metals. However, we consider useful to note that the preliminary treatment of oxides before chemisorption and calorimetric studies requires full cleaning of water and carbon dioxide from the samples (at temperatures exceeding significantly those of the subsequent experiments) and reoxidation of the samples. Only such a procedure is capable of standardizing the initial state of experimental samples and its reproduction by other researchers. Of course, H_2O and CO_2 desorption should be analyzed in the course of experiments. Therefore, the availability of rather sensitive means of H_2O and CO_2 analysis in the apparatuses intended for studies of oxide chemadsorbents is no less important than the availability of similar means in the apparatuses intended for studies of metal chemadsorbents.

1.5. Why is it urgent to generalize the technical and procedural problems of chemisorption and calorimetric studies and the ways of their solution?

The content of Section 1 shows that the difficulties arising in the course of studies of the molar heats of CHS of gases at different chemadsorbents are multiform and that available data on the molar heats of CHS should be analyzed in respect to the degree of overcoming these difficulties. The acceptance of any available unconfirmed data on molar heats of CHS without their critical analysis is superficial.

Up to the 1960s, the importance of the preliminary thermo-vacuum treatment of the samples was, as a rule, underestimated and a number of the above-listed side processes could not be revealed; although mentions on some of them were available, the methods of their consideration were not developed. Namely: (i) the hydrocarbon grease was applied everywhere; (ii) the heats of CHS measured calorimetrically at temperatures above the room temperature and the heats of CHS measured at catalysts pretreated up to the states approached to their states occurring in the course of catalytic processes were not available; (iii) the vacuum in the majority of the apparatuses intended for the calorimetric studies of CHS at films and wires was insufficient; (iv) the corresponding methods were applicable at the temperatures not exceeding the room temperature. Therefore, the not numerous CHS studies that were performed before 1960 and showed the coverage-independence of the molar heats of CHS over wide ranges of surface coverages (CHS of N_2 at $Fe/K_2O/Al_2O_3/CaO$ (isosters, up to 800 K) [14], H_2 at W (isosters, up to 800 K) [15], N_2 at W (isosters, up to 1000 K) [16], H_2 at Fe (calorimetry, 90 K) [17], N_2 at W (calorimetry, 296 K) [17], and H_2 at Ni (calorimetry, 90 and 296 K) [17]) were ignored and the ill-founded voluntary notions on surface heterogeneity gained acceptance.

By the present time, practicing calorimetrists revealed some additional technical and procedural problems in calorimetric studies of CHS in comparison with the set of such problems that was known in the early 1960s. In contrast to that time, modern technical means allow solution of these problems. However, the reviews that generalize these problems and propose the methods of their solutions are few in number. Therefore, some of available calorimetric works contain significant shortages and inadequate interpretations of measured results. Meanwhile, results of calorimetric studies of CHS are necessary for solution of the problem of “heterogeneous” vs. “homogeneous” catalytic surfaces, which is of fundamental importance to the theories of heterogeneous catalysis and CHS, and for solution of different other problems relevant to the mechanisms of different catalytic and CHS processes.

From time to time, the works that encourage the advocates of the notion on surface heterogeneity become available. Below, the results of one of such works published in [18,19] are analyzed. The authors of [18,19] studied the H_2 and O_2 interaction with iridium supported at Al_2O_3 and SiO_2 and came to the conclusion that the molar heats of H_2 CHS at Ir decrease with the surface coverage. I am forced to analyze some of questionable technical, procedural, and scientific approaches applied in this work (the techniques and procedures are detailed in [20,21]), because this work was presented by the author of [22] as the proof of surface heterogeneity of iridium.

However, it is impossible to understand, to what processes the heat effects measured in [18,19] relate. The matter is that these authors do not analyze the possibility of H_2 absorption into the iridium body and spillover of chemisorbed hydrogen to the support (Al_2O_3 or SiO_2) during or between the experiments. Meanwhile, they observed slow processes proceeding with no changes in the pressure after the fast processes and did not identify them. In addition, according to the data presented by the authors, the samples sorbed several H-atoms per one surface Ir-atom. Therefore, the occurrence of absorption, spillover, or H_2 interaction with oxygen not cleaned from the metal is apparently beyond question. It is reasonable to assume that these side processes or, at least, one of them, proceeded not only after the fast H_2 interaction with the chemadsorbent but also in the course of it. Therefore, the heat effects measured in this study do not characterize any definite process.

Works [18,19] induce also doubts with respect to the adequacy of the applied techniques and procedures. The main doubts are caused by the following. (i) The glass adsorption apparatus has no instrumental facilities allowing for controlling the degree of reduction of the samples before experiments, i.e., the water formation. Thus, the reduction is produced in the dark and, apparently, is insufficient (2 h at 723 K in H_2 under static conditions at a pressure of 0.1 MPa) because water vapor under static conditions at 0.1 MPa diffuses extremely slowly from the porous structure of the sample and hampers reduction of the surface. (ii) The combination of the pressure level and calorimetric-ampoule geometry is questionable. Indeed, the grains of the samples are not equally accessible for adsorbates (the chemadsorbent column is no less than 5 cm, the porous structure is well developed (128 and 149 m^2/g for SiO_2 and Al_2O_3, respectively) and the initial pressure in each experiment is of several tens of kilopascals). Therefore, the layer-by-layer use of adsorbents may proceed. (iii) Greased taps are applied. (iv) The renunciation of the comparative ampoule in [18,19] is quite inadmissible. It conflicts with the general idea of differential double microcalorimeters and with the experience of several generations of scientists working in the field of precise microcalorimetry. The use of identical sample, comparative, and calibrating calorimetric ampoules is especially important in precise microcalorimetric measurements of CHS because the comparative ampoules, in addition to their usual role, allow automatic subtraction of parasitical heat effects associated with admission of expansible gases into the calorimetric ampoules. The authors of [18,19] contend that they had arrived to the conclusion on the irrelevance of the use of comparative calorimetric ampoules on the basis of their experiments. Unfortunately, the experiments under consideration initiate so many questions that it is difficult to identify the causes of this erroneous conclusion.

Note that the ultra-vacuum study [23] of H_2 CHS at polycrystalline rhenium, which is similar to iridium in its physical and chemical properties, showed that the heat of CHS is equal to 128 ± 4.2 kJ/mol and that the hydrogen-desorption kinetics corresponds to homogeneous surfaces; the chemisorbed amount is equal to 6×10^{14} atoms/cm^2, i.e., it is less than that determined in [18,19] by a factor of several units and is limited by the monolayer capacity.

Works [18,19] show that generalization of the principal technical and procedural problems of calorimetric and chemisorption studies is urgent. Understanding of all these problems in the aggregate and development of the methods for their solution take a considerable amount of time and require a rather wide practical experience. This understanding is necessary not only to the researchers working in the fields of CHS and calorimetry but also to the specialists in related fields, because indiscriminate using of CHS and calorimetric data may lead to erroneous conclusions and ungrounded movements.

2. The progress in studies of the molar heats of chemisorption of gases at metals

2.1. The "homogeneity" vs. "heterogeneity" problem and importance of data on the heats of chemisorption for its solution

The problem of "homogeneity" vs. "heterogeneity" of surfaces of catalysts and adsorbents has a long history. Great I. Langmuir was the first to introduce the notion on heterogeneous surfaces [24]. However, Langmuir wrote that the surfaces of crystal bodies consist of centers of one or two types and that the centers of any one type have the same CHS activity. He believed that all surface adsorption centers can be different in their CHS activity only at unstructured amorphous bodies, such as glasses, and never applied the concept on heterogeneous surfaces (in his terminology: amorphous surfaces) to crystal bodies.

Later researches developed the hypothesis, according to which surfaces of catalysts and chemisorbents are heterogeneous and, allegedly, this heterogeneity reveals itself in CHS equilibriums (for example, in the so-called logarithmic isotherm) and in kinetics of catalytic processes (in kinetic equations involving pressures to fractional powers). This hypothesis was first applied in catalysis in [25]; it was shown that the ammonia synthesis kinetic equation, which follows from the empiric kinetics given by Benton [26] and Winter [27] for ammonia synthesis and destruction, respectively, can be deduced on the basis of a reaction mechanism including the notion on surface heterogeneity. We can not detail this hypothesis and present its short formulation given by Kiperman [28], who was one of the authors of the concept of heterogeneous surfaces and advocated this concept in his discussion with Boudart in 1989 [29]. The formulation of the hypothesis of surface heterogeneity was given by Kiperman in [30], where he argued against Roginskii [31], who criticized the notions of [25] on the mechanism of ammonia synthesis.

Roginskii wrote in [31] that (i) any wide distribution of surface centers by their reaction ability leads to the same kinetic equation; (ii) the physical postulates of the hypothesis are very hazy; (iii) the derivations of the equations are not always generalized adequately and are excessively sophisticated; (vi) the deduced equations are apparently not the unique ones compatible with the experimental data.

Answering the point (ii) of this criticism, the author of [30] wrote that "... only the linear and exponential distributions of the centers of heterogeneous surfaces (he meant the linear or exponential decrease in the molar heats of adsorption with the coverage) can lead, under the occurrence of the linear relation (between the variations in the heats of CHS and the activation energy of CHS), to the kinetic equations involving pressures to fractional powers." Just this elucidation is the shortest and most intensional formulation of the hypothesis of surface heterogeneity.

The author of [30] and other advocates of the hypothesis on surface heterogeneity believed that the kinetic equations involving pressures to fractional powers can be deduced exclusively from the notions on surface heterogeneity and that, therefore, the applicability of these equations to description of experiments on the effect of different reactants on the rates of catalytic reactions is the proof of heterogeneity of the catalyst surfaces; Temkin wrote this statement in [25] and repeated it in a number of subsequent papers.

However, we showed the following [32]. The fractional-order kinetic equations for the processes of ammonia synthesis at $Fe/K_2O/Al_2O_3$, methanol synthesis at ZnO/Cr_2O_3, shift-reaction and carbon exchange between CO and CO_2 at Fe_2O_3, SO_2 oxidation at Pt, and carbon exchange between CO and CO_2 at Fe_2O_3 that were deduced earlier from the notion on surface heterogeneity can be also deduced from the notion on surface homogeneity. Besides, if the kinetics of a catalytic reaction can be described by a kinetic equation containing reacting-components pressures to fractional powers, that's not to say that another kinetic equation containing no pressures to fractional powers and deduced from notions on surface homogeneity is in capable of describing the same kinetic data. Analogously, the satisfiability of the Elovich equation for the CHS rates does not mean that the adsorbing surface is heterogeneous; the same interdependence between the adsorption rate and the adsorbed amount is characteristic for adsorption at homogeneous surfaces of molecules that occupy more than one surface center [32]. We showed [32,33] that the pressure–coverage dependence transmitted by the logarithmic isotherm can be also transmitted by the isotherms deduced from the notion on surface homogeneity. Boudart and Djega-Mariadassou [34,35] showed that any file of kinetic data can be described by several kinetic equations different in their form. These ideas were developed in [36]. According to these works, similar mathematical behavior of the rates of catalytic reactions can be obtained on the basis of notions on homogeneous and heterogeneous surfaces. An analogous conclusion relative to different two-step reactions was made by us in [32,37–40]. We don't consider here the problems relating to description of the kinetics of catalytic reactions. However, we note that our conclusions on applicability of the concept of homogeneous surfaces to description of the kinetics of catalytic processes and chemisorption equilibriums are rather close to the conclusions published in [29,34–36]. We believe that the disagreements are mainly terminological and are removable. We see only one more or less significant discrepancy in the approaches to the theory of kinetics of catalytic processes; this is the notion on the structure-sensitive and structure-insensitive reactions. I doubt that such a classification of stationary catalytic reactions proceeding at real catalysts is sufficiently justified, because the crystal faces are affected with time by catalytic reactions and the surface structure is apparently dictated by the catalyst–reacting medium system rather than by the structure of the initial solid sample. By the way, these authors note that such a classification is debatable, that there are reactions that do not seem to be easily classified in this manner ([35], p. 91). This debatable question requires detailed consideration, which is beyond the scope of this review.

The works cited in Section 2.1 (see also [5]) show that no formalism is capable of solving the "homogeneity" vs. "heterogeneity" problem. Therefore, the results of measurements of the molar heats of CHS are of prime importance for solution of this long-discussed problem and the molar heats measured at the catalysts maximum approached to their states occurring in the course of real catalytic processes are of special interest.

Before proceeding to the available data on the heats of CHS and in the context of the occurrence of the technical and procedural problems considered in Section 1, we note the following. It is unlikely that any coverage-dependent molar heats could be transformed by overlooked side processes to the coverage-independent ones. Meanwhile, different side processes can produce an illusion that the heat of CHS decreases with the coverage. Therefore, the coverage-independent results of measurements of the molar heats of CHS provoke less technical questions and look more convincing than the coverage-dependent ones.

Just below, we list the systems in which coverage-independent or almost coverage-independent molar heats of CHS are obtained for rather wide ranges of surface coverages. The results of another kind are also available. However, we will give a number of examples demonstrating that the more recent is the study and the more attention is given to the adsorption and calorimetric techniques and procedures, the smaller is the angle between the abscissa and the heat–coverage function. We consider the CHS freed from side processes as the two-dimensional phase transition. In the general case, it includes three successive chemical steps of formation of crystallization centers, of two-dimensional phase I, and of two-dimensional phase II (e.g., M_2A and MA, respectively; M is a surface metal-atom and A is an adsorbate atom); therewith, each step is characterized by a definite heat effect and the heat effect for phase II formation is smaller than that for phase I formation. In practice, the first step may manifest itself not at all, because the calorimetric sensitivity is limited, and the third step may be absent or may be so slow that its heat effect cannot be measured. (Notice that we say about the heat effects of CHS not influenced by sintering of the samples; to avoid sintering, the samples should be heated before calorimetric measurements.)

H_2 at Fe [17,41,42,43], $Fe/K_2O/Al_2O_3$ [11,13], Ni [17,44,45], Pt (black) [46], Pt/SiO_2 [47], $Pt/W/SiO_2$ [47], Pt [48], Pt (powder) [49], Ce, Dy, Lu, Er, Tm, and Yb [50], W [15];

O_2 at Fe [51,52], Ni [52], $Pt/W/SiO_2$ [47], Nb [52], W [52], Mn [52], Co [52,53], Mo [52], Ta [52], Ti [52], Cu [5,54–56], Ag [57,58], W/SiO_2 [47], and Au [59];

N_2 at Ni [60], $Fe/Al_2O_3/K_2O$ [13,14], and W [16,17];

CO at Ni [45], Cu-component of $ZnO/Cu_4(OH_2)/Al_2O_3$ [61,62], Dy [63], Ni (powder) [64], Ni/K (powder) [64], Ni/Cs (powder) [64], Pt (powder) [64], Pt/Rb (powder) [64], and Pt/Cs (powder) [64];

$CH_2{=}CHCOOH$ at V/Mo, V/Mo/Cu, V/Mo/P, and V/Mo/Cs [65];

C_2H_2 at Pt [49,66];

$H_3C(C{\equiv}CH$ at Pt [66];

C_2H_4 at Pt (powder) [49], Co/Mg/Mo, Ni/Mg/Mo, Cu/Al_2O_3, Ti, and Ag [67];

C_3H_8 at Co/Mg/Mo, Ni/Mg/Mo, Cu/Al_2O_3, Ti, and Ag [67].

Let us consider some of the systems in more detail.

2.2. The effect of improvement of the techniques and procedures

In Section 1, we showed that correct revealing of the molar heats of CHS is a rather difficult experimental task. It is quite natural that the effect of technical and procedural improvements reveals itself in the results of measurements of the molar heats of CHS, and it is also natural that some works fall out of the general tendency. Therefore, any one calorimetric work can not solve the problem of "heterogeneity" vs. "homogeneity" of thermally stabilized surfaces of catalysts and chemadsorbents.

The results given below demonstrate the general effect of improvement of the experimental techniques and procedures on the available values of the molar heats of CHS and on the fundamental conclusion about homogeneity of surface centers of thermally stabilized metal surfaces.

In 1966, Bröcker and Wedler published the results of measurements of the molar heats of H_2 CHS at Ni-films in an ultra-vacuum apparatus [44]. It was shown that the heat of CHS is coverage-independent up to almost full coverage of the surface. These authors presented a figure (Fig. 2), in which they plotted their own data and the data obtained for the same process by other authors [68–72] in 1950, 1953, 1957, 1960, and 1964. It turned out that, the fresher are the data, the smaller is the angle between the measured dependence and the abscissa; only one curve falls out of this regularity. It is obvious that this effect results from progressive improvements of the adsorption and calorimetric techniques and procedures.

The analogous conclusion can be made for some other adsorbent/adsorbate systems. In 1966, we published the molar heats of O_2 CHS at silver powder [73]. It was our first calorimetric work and the first adsorption-calorimetric work performed at heightened temperatures. The measurements were performed on the basis of adsorption procedures characteristic for the early 1960s. We obtained the heats of CHS decreasing with the surface coverage.

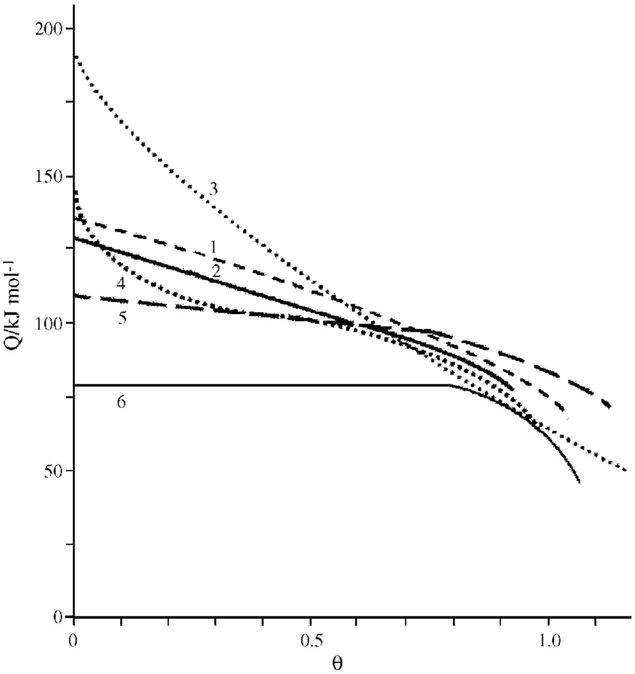

Fig. 2. Heats of H_2 chemisorption at Ni-films at 273 and 298 K: (1) 1950 [68], (2) 1953 [69], (3) 1957 [70], (4) 1960 [71], (5) 1964 [72], and (6) 1966 [44]; at monolayer chemisorption, $\theta = 1$.

After improvement of the methods and procedures, we repeated measurements of O_2 CHS at Ag and obtained a two-level curve consisting of two coverage-independent sections of about 200 and 70 kJ/mol connected by a transition curve [57] (Fig. 3). A similar heat–coverage dependence was obtained for this system by Czanderna [58] on the basis of his measurements of the CHS isosters in ultra-vacuum apparatus. These two works show that Ag surfaces are really homogeneous and that O_2 chemisorbs in two forms (apparently, O^{2-} and $O_2{}^{-}$), the latter arising once the former covers the surface. The details are given in [7,57], where the reaction of H_2 with chemisorbed oxygen and the heats of H_2 CHS at oxidized surface are also considered.

As was shown in Section 1.3, grease-vapor oxidation to CO_2 and H_2O and other side processes at the Ag surface made the major contribution to the heat effect measured in [73]. The adsorption techniques and procedures characteristic for the mid-twentieth century led many researchers to erroneous results (see [7]). The sources of these errors and the ways of their elimination are analyzed in Section 1 of this review.

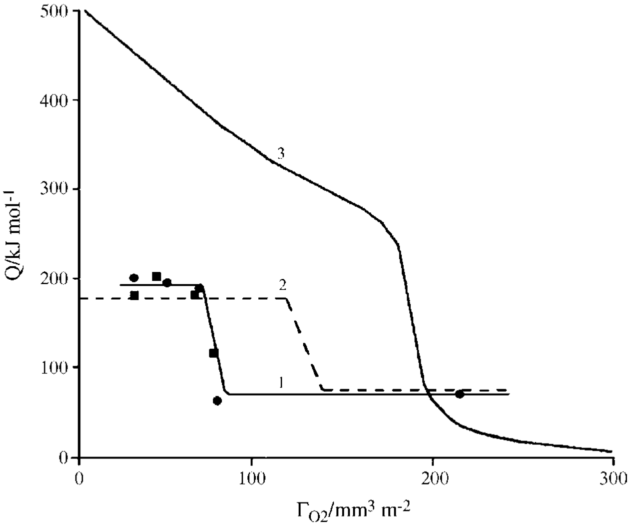

Fig. 3. Heats of oxygen chemisorption at Ag-powders: (3) 1966, 373 K [73]; (2) 1977, from isotherms, 450–615 K [58]; (1) 1979, 465 and 469 K [57].

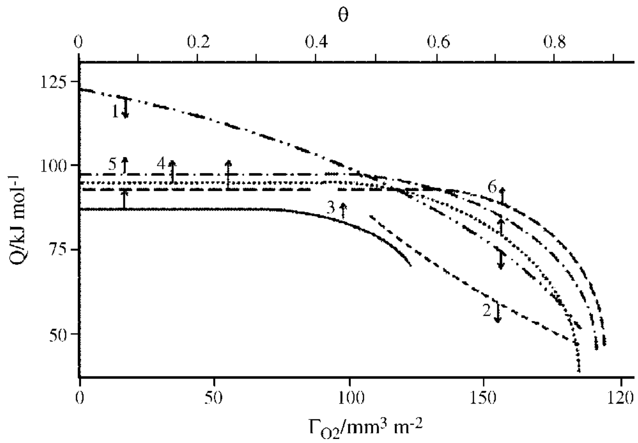

Fig. 4. Heats of H_2 chemisorption at Fe-films at 273 and 298 K: (1) 1950 [74], (2) 1953 [75], (3) 1972 [41], (4) and (5) 1978 [43], and (6) 1990 [42].

One more example of such a kind is the history of measurements of the molar heats of H_2 CHS at iron films (Fig. 4). In the 1950s, coverage-dependent molar heats of H_2 CHS were obtained [74,75]; however, since 1972, it was repeatedly shown that the heats of CHS at about room temperature do not depend on the surface coverage over a wide range of its variation [41–43].

We see that the fresher are the data, the more homogeneous are the surfaces.

2.3. *Results of adsorption and calorimetric studies of chemisorption at industrial catalysts approached to their states occurring under conditions of catalytic processes*

In this section, we consider the results obtained with industrial catalysts of the processes of NH_3 synthesis and CH_3OH synthesis: the Fe/0.083 K_2O/0.033 Al_2O_3/0.038 CaO catalyst SA-1 [11] and the ZnO/0.50 Cu_4 (OH_2)/0.14 Al_2O_3 catalyst SNM-1 [10], respectively; the samples were obtained from the Severodonetsk Chemical Industrial Complex (Ukraine). The methods, techniques, and procedures used for preliminary treatment of the catalysts and for performance of the experiments are detailed in the reviews [5,7,10,55,76] and original works [11,13,61,77–81].

From the start of the pretreatment and to the end of the experiments, each of the samples had no contact with the atmosphere. The apparatuses and procedures are detailed in [7,10].

The $Fe_2O_3/K_2O/Al_2O_3$/CaO catalyst was reduced by the H_2(10%)/He(90%) gas mixture at a volumetric flow rate of 15000 h^{-1} for 200 h at 823 K with controlling of H_2O desorption up to its full cleaning from the sample and was degassed for 55 h at 823 K. The available calorimetric and adsorption instrumentation does not allow for measuring the molar heat effects of N_2 CHS at powdery iron catalyst, and, therefore, such measurements had never been performed. In [13], the heats of N_2 CHS were calculated from the heats of NH_3 decomposition with desorption of nitrogen on the basis of measurements performed at 470 K [13]. The molar heats of N_2 CHS (Q_{N2}, kJ/mol) were calculated from the equation

$$Q_{N2} = 98.3 + (q - nQ_{H2})/m, \tag{4}$$

where 98.3 (kJ/mol) is the tabulated heat effect of decomposition of two moles of NH_3 to gas H_2 and N_2 at a constant pressure, q (kJ) is the heat amount evolved during the experiment, Q_{H2} (kJ/mol) is the molar heat of H_2 desorption from the chemisorbed hydro-

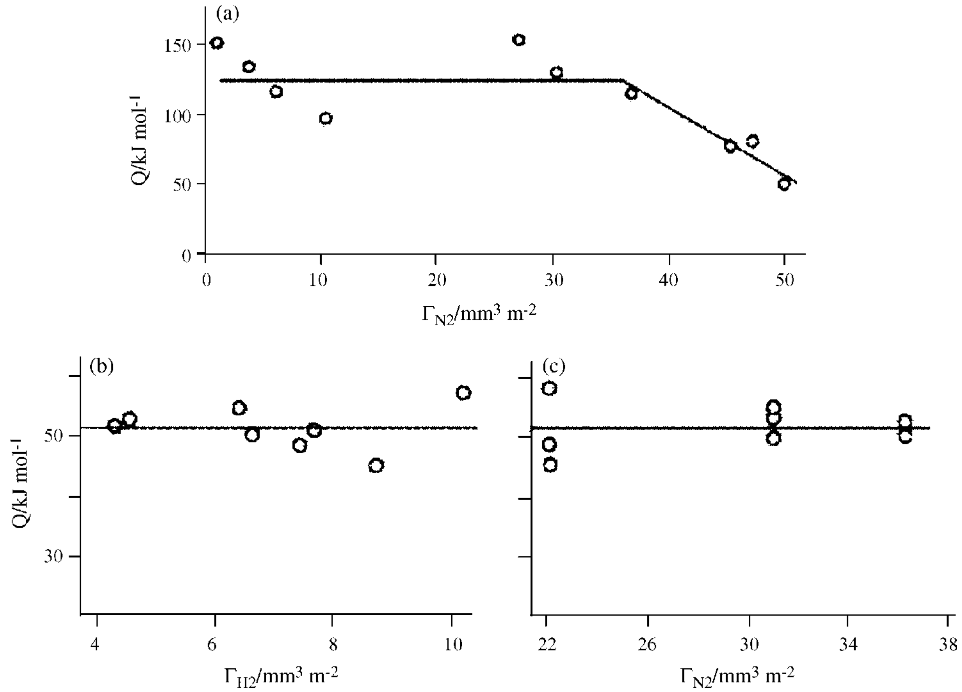

Fig. 5. Heats of chemisorption at a Fe/K_2O/Al_2O_3 catalyst at 470 K: of N_2 vs. coverage by nitrogen (a) and of H_2 vs. coverages by hydrogen (b) and nitrogen (c) [13,11,5,77].

gen/nitrogen radicals, and *n* and *m* are the moles of hydrogen and nitrogen chemisorbed in the form of hydrogen/nitrogen radicals, respectively. It was stated preliminary that nitrogen at catalyst surface at around 470 K is bound almost entirely with surface hydrogen when the N/H ratio at the carefully degassed catalyst is rather high and that the heat of decomposition of hydrogen/nitrogen radicals to gas H_2 and chemisorbed nitrogen $Q_{H2} = 51.5$ kJ/mol. To calculate Q_{N2}, four parameters should be measured. The errors in the measurements of *q*, *n*, *m*, and Q_{H2} were equal to 1–2, 7–10, 7–10, and about 7%, respectively. Note that such measurements performed with catalyst weights of about 1 g, in line with the recommendations described in Section 1, would be very problematic without the apparatus presented in Fig. 1.

In Fig. 5a, the molar heats of N_2 CHS are given.

Fig. 5b and c present the molar heats of decomposition of surface hydrogen/nitrogen radicals into gaseous hydrogen and chemisorbed nitrogen (the molar heats of H_2 desorption from the catalyst surface covered with hydrogen/nitrogen radicals). The molar heat of H_2 desorption depends neither on the nitrogen content (Fig. 5c) nor on the hydrogen content (Fig. 5b) at the catalyst surface. Although the data scattering in Fig. 5a–c is significant, the experimental results presented in these figures show that the surface is homogeneous.

Thus, the surface homogeneity of the Fe/K_2O/Al_2O_3/CaO catalyst is demonstrated twice, by the measurements of the heats of N_2 and H_2 CHS at the surfaces containing both nitrogen and hydrogen.

We see that the surface of industrial Fe-containing catalyst is homogeneous likely to the surface of Fe-films (see Fig. 4). Note that the homogeneity of Fe-containing catalysts was repeatedly proved by different other measurements. Namely, the isosteric molar heats of N_2 CHS at the Fe/K_2O/Al_2O_3/CaO catalyst [14] (it should be noted that these measurements were performed in a rather narrow range of surface coverages), calorimetric molar heats of O_2 CHS at Fe-films [51,52] (see Section 2.4), and activation energy for N_2 [82–84] desorption from Fe-films are coverage-independent and the rate of N_2 desorption from individual Fe crystal planes is proportional to the surface coverage [82–84].

This collection of information on CHS of different gases at iron, apparently, leaves no doubts in homogeneity of iron surface.

The ZnO/0.50 Cu_4 (OH_2)/0.14 Al_2O_3 catalyst was pretreated as follows. Under vacuum, the source sample was heated in the glass apparatus (with a trap cooled to 77 K) at temperatures increased stepwise up to 723 K for about 115 h, including about 50 h at 673 K and about 30 h at 723 K. Upon completion of H_2O and CO_2 desorption, the catalyst was oxidized with O_2 at 623 K and 13 hPa. Then, the catalyst was reduced very slowly at no more than 473 K and at an H_2 or CH_3OH pressure of about 1 hPa. The reduction was continued up to a state, at which introduction of a $(CO_2 + H_2)$ mixture or H_2 into the degassed volume over the catalyst led to methanol formation or did not lead to H_2O formation, respectively.

The table contains the results of measurements of the molar heats of H_2 CHS at the ZnO-component and of CO CHS at the $Cu_4(OH_2)$-component of the ZnO/$Cu_4(OH_2)$/Al_2O_3 catalyst. The molar heats of H_2 and CO CHS are coverage-independent and are equal to 46.44 ± 4.13 and 65.83 ± 4.75 kJ/mol, respectively. Before each of these experiments, the catalyst surface did not contain the adsorbate under study. It is seen that the variation in the amount of chemisorbed hydrogen by a factor of 12.5 (from 12 to 125 μmol per 1 g of the catalyst) does not change the molar heat of H_2 CHS at the ZnO-component and the variation in the amount of chemisorbed carbon monoxide by a factor of 13.7 (from 2.4 to 33 μmol per 1 g of the catalyst) does not change the molar heat of CO CHS at the $Cu_4(OH_2)$ component of this catalyst.

It was stated that the kinetics of O_2 and CO_2 CHS at the $Cu_4(OH_2)$- and ZnO-components, respectively, obeys the equation

$$r = kp\left[1 - \left(\frac{\Gamma}{\Gamma_\infty}\right)\right]^2 \cdot \left\{\frac{z}{[z - (\Gamma/\Gamma_\infty)]}\right\} \tag{5}$$

r is the CHS rate, *p* is the pressure, Γ is the chemisorbed amount, Γ_∞ is the monolayer CHS. This equation is a particular case of our theory that considers the rates and equilibriums of CHS of the substances, each molecule of which occupies more than one surface center at homogeneous surfaces [33,85,86]. Eq. (5) corresponds to the CHS of each molecule at two surface centers of the /1 0 0/ crystal face.

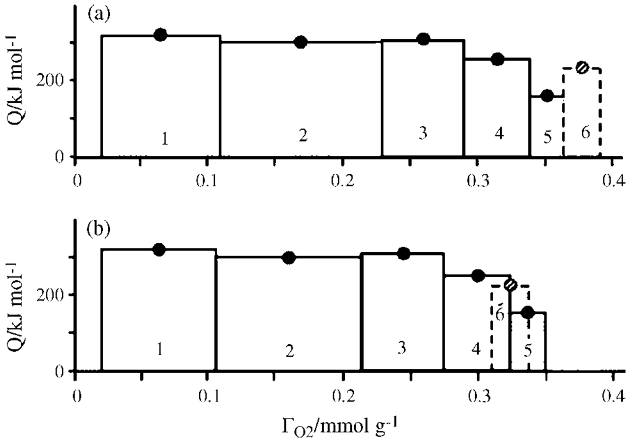

Fig. 6. Molar heats of O_2 chemisorption at $Cu_4(OH_2)$-component of $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst vs. chemisorbed amount (293 K); (a) without consideration of O_2 diffusion into the sample body for the time interval of 90 h between the experiments 5 and 6; (b) with consideration of O_2 diffusion into the sample body.

Fig. 6 gives the molar heats of O_2 CHS at the $Cu_4(OH_2)$-component of the $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst (the grounds allowing us to specify the $Cu_4(OH_2)$ composition for the Cu-component of the catalyst and to relate the O_2 CHS to just this catalyst component are given in [10,55]). Note that the initial O_2 portion (up to a degree of coverage of 5.7%; it is not shown in the figure) chemisorbs with a molar heat effect of about 485 kJ/mol. The heat of O_2 CHS at higher coverages (O_2 portions 1–4 in Fig. 6a) is constant, the rate of CHS in each of the portions is proportional to the pressure, and the rate–coverage dependence is described by the kinetic equation corresponding to CHS of each molecule at two surface centers of homogeneous surfaces up to the region of surface saturation [61]. This means that the $Cu_4(OH_2)$ surface is homogeneous and that the rate-determining step of CHS is O_2 interaction with two surface centers. To the end of portion 5, the kinetic order of CHS and the molar heat of CHS decreased. Apparently, this means that the rate of CHS at the surface covered almost completely by oxygen depends on the rate of formation of paired surface centers and that some of oxygen molecules chemisorb in the molecular form with a small molar heat effect. However, after the 90-h aging of the sample in vacuum at 293 K, it was found that the sample is capable of chemisorbing an additional O_2 amount with an enhanced molar heat of CHS (portion 6). After portion 6, the rate of O_2 CHS was so small that it cannot be measured. This additional O_2 CHS results from oxygen diffusion into the sample body from the surface. Apparently, no other cause, but diffusion of chemisorbed oxygen into the sample body, exists for this additional CHS with the observed increased molar heat effect. Fig. 6b is designed with allowance for the effect of oxygen diffusion. When transforming Fig. 6a into Fig. 6b, it was taken that the rate of oxygen diffusion into the sample body is proportional to the degree of coverage and to the duration of the aging and the corresponding corrections for oxygen diffusion into the sample body from each chemisorbed portion of oxygen were introduced. The position of the point corresponding to the molar heat of O_2 CHS in portion 6, apparently, confirms the correctness of our conclusions.

Closely equal results were obtained by us [56] and by the authors of [54] for O_2 CHS at powder Cu and at Cu-film, respectively (see [5]). It is seen that the real $Cu_4(OH_2)$ surface of this composite catalyst is homogeneous.

Thus, the surface homogeneity of the $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst is proved five times, by the measurements of the molar heat of O_2, H_2, and CO CHS and of the rates of O_2 and CO_2 CHS.

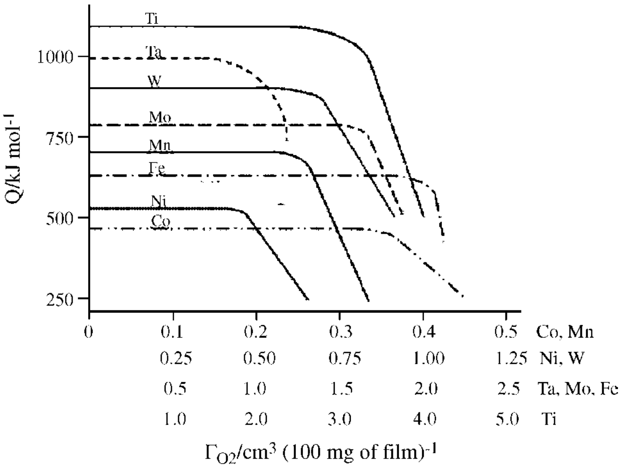

Fig. 7. Molar heats of O_2 chemisorption at evaporated films of different metals vs. chemisorbed amounts, 273 K [52].

The content of this subsection shows that the measurements of the CHS heats and rates not influenced by side processes testify that real surfaces of different catalysts are homogeneous in their CHS ability; at least, these measurements give no grounds to say that any heterogeneity reveals itself in the heats or rates of CHS.

2.4. *Examples of the heats of O_2 chemisorption*

Fig. 7 presents the results of one of the first ultra-vacuum calorimetric measurements [52] of the heats of O_2 CHS at metal films. This work was performed at 273 K, when the oxygen surface–body diffusion is hardly significant. It is seen that the molar heats of O_2 CHS at eight metals are constant over wide ranges of surface coverages; thus, the surface of each of these metals reveals itself as the homogeneous one.

Later [53] (see also [5]), we measured the heats of O_2 CHS at Co-powder at 298 K and confirmed the corresponding results of [52].

Fig. 8 presents the molar heats of O_2 CHS at Cu-powder (373 and 383 K) [56], Cu-component of the reduced powder $CuO/ZnO/Al_2O_3$ catalyst (293 K) [5], and Cu-film (298 K) [54]. For the densest crystal face /111/, monolayer CHS in the form of Cu–O (ads) corresponds to about 130 mm^3 O^2/m^2. It is seen that dependences of the same form are obtained for these three copper systems. They correspond to

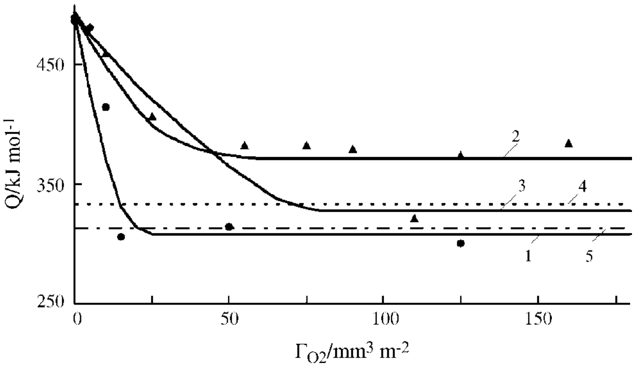

Fig. 8. Molar heats of O_2 chemisorption at Cu: curve 1 and circles [5] represent the results of measurements performed with the reduced copper component of the $CuO/ZnO/Al_2O_3$ catalyst by using a FOSKA calorimeter; curve 2 and triangles [56] represent the results of measurements performed with the reduced Cu powder by using a FOSKA calorimeter; curve 3 [54] represents the data obtained with the Cu film under ultra-vacuum. Dashed lines 4 and 5 represent the $\Delta H^0{}_{298}$ values for the reactions $O_2 + 4Cu = 2Cu_2O$ and $O_2 + 2Cu = 2CuO$, respectively.

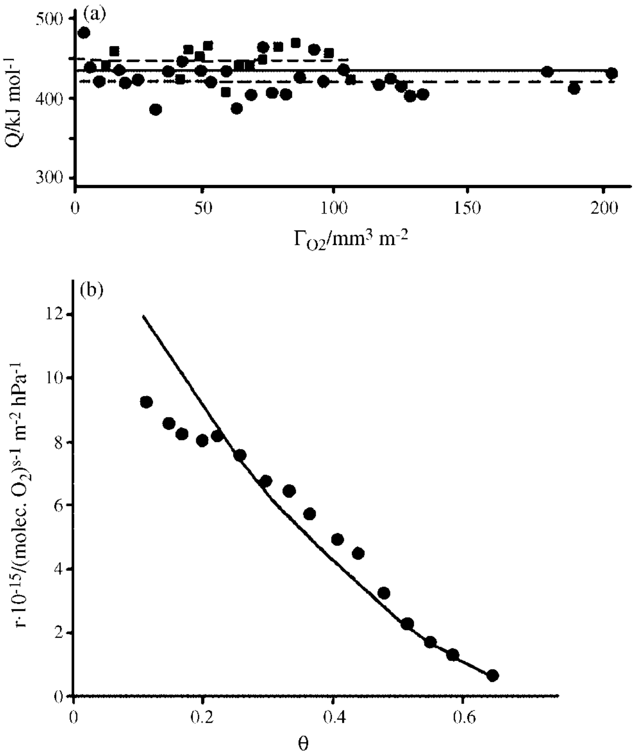

Fig. 9. (a) Molar heats of O_2 chemisorption at powdery Au vs. chemisorbed amount [7,59]: sample 1 (413 K), circles; sample 2 (393 K), squares; lower and upper dashed lines give the mean *Q* for samples 1 and 2, respectively; solid line gives the overall mean *Q*; (b) rate of O_2 chemisorption at powdery Au vs. surface coverage [85], sample 1 (413 K): points are experimental values, curve is calculated by Eq. (6) ($n = 4$, $z = 6$).

formation of the nuclei of the oxygen chemadphase (chemisorbed surface phase; detailing see in [10]) with an enhanced molar heat effect in a rather narrow range of surface coverages and to CHS with a constant molar heat effect up to CHS of, at least, 70% of one monolayer. The high molar heat effect observed at the start of CHS can not be explained by any side process because the similar effect was repeatedly observed in different Cu-systems in experiments with powders under usual vacuum and with films under ultra-vacuum [5,54,56]. This heat effect can not be explained either by the hypothesis on surface-Cu_2O formation forerunning surface-CuO formation. Indeed, the difference between the initial (about 485 kJ/mol) and most abundant (about 305 kJ/mol) molar heat effects is very high and, therefore, if these two processes occurred, the first of them would be much more preferable thermodynamically and, if it began, it would proceed up to full coverage of the surface.

It is also seen that the levels of the horizontal sections of the curves differ not very significantly from the level characteristic for Cu_2O formation.

Fig. 9 relates to O_2 CHS at gold powders. The calorimetric results (Fig. 9a) are obtained in two series of experiments performed with two samples at 413 and 393 K; they testify unambiguously that the real gold surface after a prolonged reduction by H_2 and thermo-vacuum treatment is homogeneous (the details are given in [7,59,85]).

For some adsorbent/adsorbate systems, the rate of CHS decreases with surface coverage quicker than $(1 - \theta)$ (θ is the degree of surface coverage). Advocates of surface heterogeneity consider such experimental data as a support for the concept of surface heterogeneity. Work [85] was used to show that the rates of CHS should decrease much quicker than $(1 - \theta)$ at homogeneous surfaces if each adsorbate molecule occupies several adsorption centers. It was shown that the rate (r_+) of CHS proceeding with formation of mobile films consisting of nondissociated admolecules or of dissociated ones and migrating as a single whole is described by the equation [32,33,85,87]

$$r_+ = \alpha'(n,\ z)\alpha'_0\, p(1-\theta)^n \left\{\frac{z}{[z-(n-1)\theta]}\right\}^{n-1} \qquad (6)$$

Here, α'_0 and α' are constants, the last being a function of n and z; p is the pressure; n is the number of the surface CHS centers covered with a chemisorbed molecule; and *z* is the number of the CHS centers that would be covered with a chemisorbed molecule when we mentally rotate it by 360° in the surface plane around any CHS center at which this molecule is mentally fixed. For example: $n = 6$ for the /1 1 1/ face of a face-centered cubic lattice and $n = 4$ for the /1 0 0/ face of a simple cubic lattice; and $z = 18$ for CHS of benzene (at seven CHS centers) at the /1 1 1/ face of a face-centered cubic lattice and $z = 8$ for CHS of two paired O-atoms (at four CHS centers arranged as a square) at the /1 0 0/ face of a simple cubic lattice.

In Fig. 9b, the points are the experimental CHS rates and the solid curve is calculated for the case of CHS of each O_2-molecule at four surface centers of the /1 1 1/ face of a face-centered cubic lattice ($n = 4$, $z = 8$) in the form of O-atoms, each of which occupies two surface centers. It is seen that the curve corresponds to experimental data and describes the r_+ decrease by a factor of about 15 when the $(1 - \theta)$ value decreases by a factor of about 3 (from 0.9 to 0.3).

Note that Eq. (6) is not exact. It was deduced in [85] in the Bethe approximation; it contains parameter *z* that is different for different crystal faces and, really, is not constant for polycrystalline samples. Therefore, there are no grounds to expect the exact description of the rate of CHS at polycrystalline surfaces by this equation. It is applied to show that the rate of CHS can decrease with θ at homogeneous surfaces much quicker than $(1 - \theta)$. Indeed, it is seen that the θ-dependence of r corresponds rather well to CHS of each O_2 molecule at four surface centers of the /1 1 1/ face of cubic crystals.

The statistical methods of description of CHS of the substances, each molecule of which occupies several CHS centers at homogeneous surfaces, and the mode of applications of these methods are detailed in [32,87,88]. In [32,87], original equations of isotherms for the following mechanisms of multicentered CHS at homogeneous surfaces are considered: (i) formation of mobile films consisting of nondissociated molecules or of dissociated ones and migrating as a single whole; (ii) CHS of two-atom molecules with their dissociation and formation of chemisorbed films, where each chemisorbed atom occupies two surface centers and the atoms migrate on the surface independently of one another; (iii) CHS of two-atom molecules at two surface centers without dissociation of the admolecules or with their dissociation and migration of the two atoms together, or with dissociation of the admolecules without migration of the adatoms; and (iv) dissociative CHS of two-atom molecules with formation of mobile films, where each atom occupies one center. In these references, the corresponding equations for the *r*–θ dependences are also considered.

Let us also pay attention to the statistical coefficient α' (n, z). This coefficient is constant for any concrete system and depends on the arrangement of surface atoms of the adsorbent and on the configuration of the chemisorbed particles. For benzene CHS at the /1 1 1/ face, it is about 10^{-4}; at $n = 2$ it is equal to several units. Thus, the CHS rate for the molecules occupying several surface centers in one CHS act can not be equal to the number of molecular collisions with the surface [85].

2.5. Examples of the heats of CO chemisorption

We showed (see Table 1) that the molar heat of CO CHS at $Cu_4(OH_2)$-component of the catalyst of the methanol synthesis

Table 1
Molar heats of H_2 CHS at the ZnO-component and of CO CHS at the $Cu_4(OH_2)$-component of the $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst.

System	Experiment number	Temperature (K)	H_2 chemisorbed (μmol/g)	Molar heat, *Q* (kJ/mol)
H_2/ZnO-component	1	298	16	41
	2	298	12	46
	3	303	15	40
	4	303	13	49
	5	303	13	43
	6	293	14	49
	7	323	14	51
	8	353	12	50
	9	323	125	49
$CO/Cu_4(OH_2)$-component	1	303	13	60
	2	353	33	67
	3	303	12	67
	4	303	2.4	67
	5	303	5.8	73
	6	303	9.2	61

and shift-reaction is coverage-independent. Consider other examples.

Fig. 10 demonstrates the results by Dumesic and Spiewak [64] on CO CHS at 308 K at three powder samples prepared on the basis of nickel. For each of the samples, the molar heats of CO CHS are coverage-independent (within the possible experimental deviations) over a wide range of surface coverages, and thus the surfaces of the samples are homogeneous.

Work [64] also contains no less demonstrative data on CO CHS at 403 K at surfaces of platinum and of Cs-promoted and Rb-promoted platinum samples calcined in O_2 and then reduced in H_2 and degassed. The surface of each of these samples is homogeneous, and the molar heats of CHS and the CHS capacities per unit mass are approximately the same.

The list given at the end of Section 2.1 presents also other examples of CO CHS.

Note the following. Two-level curves with transition branches lying between two heat levels are typical for CHS proceeding in two forms, one of which is thermodynamically preferable and forms at the first step up to full or almost full surface coverage. Therewith, the second, weakly-bound adsorbed form can be associated with absorption or surface transformation of chemisorbed particles with compacting of the chemisorbed layer. Besides, different side processes reveal themselves most clearly at the initial or final steps of CHS processes; therefore, CHS proceeding just over middle coverages is most informative for conclusions on the degree of homogeneity of surfaces.

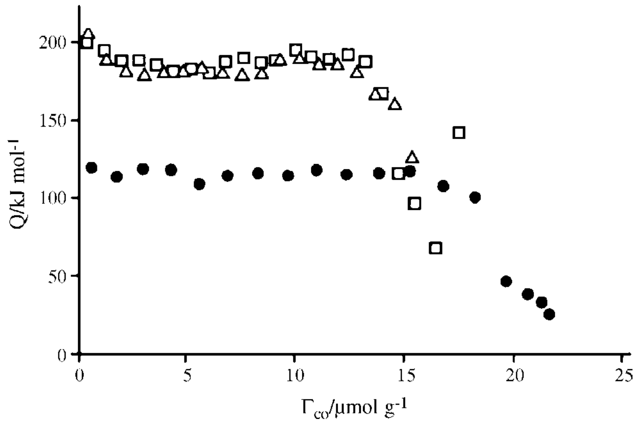

Fig. 10. Molar heats of CO chemisorption at powders (308 K): Ni (circles), Ni/K (squares), and Ni/Cs (triangles) vs. chemisorbed amounts [64].

2.6. Examples of the heats of chemisorption of hydrocarbons

Notice that coverage-independent molar heats of CHS were obtained even for CHS of some hydrocarbons, i.e., of the substances that, according to some opinions, can chemically interact with metal surfaces at room temperature. Fig. 11 gives the heats of acetylene and methylacetylene CHS at Pt-films [66].

Works [49,64] contain no proofs for the completeness of reduction of the samples and for the absence of CO_2 and H_2O desorption in the course of each experiment and between them. However, the side processes associated with surface–body diffusion, surface reactions, and desorption of the side products did not reveal themselves under rather low temperatures at which these studies were performed. The results of these works are quite sufficient for the surfaces of the studied adsorbents to be considered as homogeneous, because the molar heats of CHS over rather wide ranges of surface coverages are constant within the experimental errors (Fig. 12).

Several examples of ethylene and propylene CHS at different oxide catalysts are given in Fig. 13 [67]. These examples are rather demonstrative.

2.7. Examples of the heats of H_2 chemisorption

We presented the works showing that surfaces of Ni (Fig. 2), Fe (Figs. 4 and 5), ZnO-component of the $ZnO/Cu_4(OH_2)/Al_2O_3$ cat-

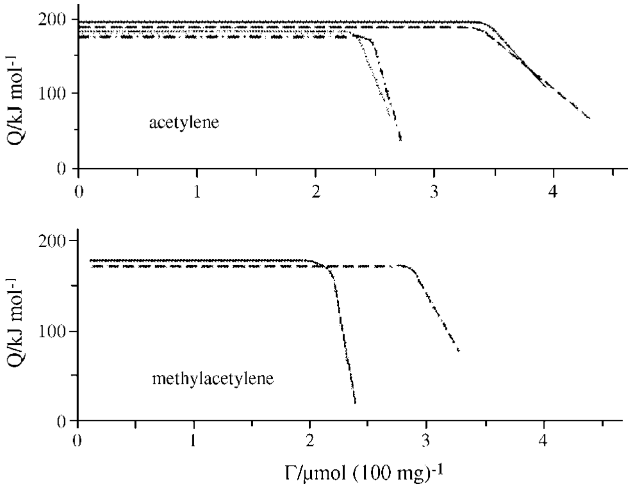

Fig. 11. Molar heats of C_2H_2 and HC_2CH_3 chemisorption at Pt films vs. chemisorbed amounts (room temperature, measurements with different samples) [66].

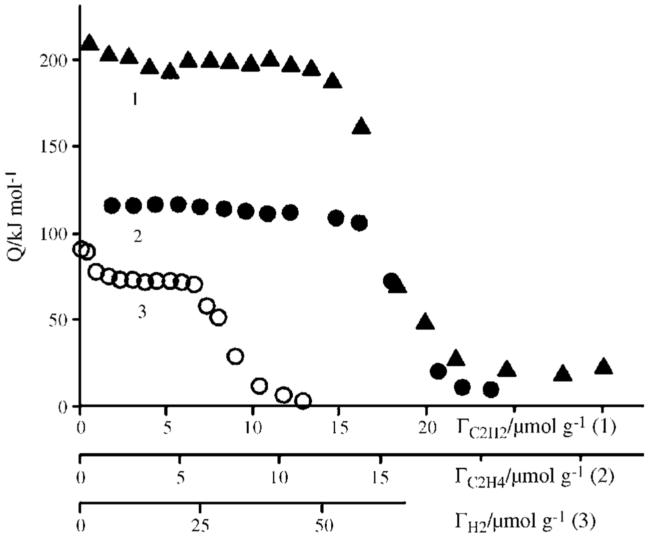

Fig. 12. Molar heats of C_2H_2 (1), C_2H_4 (2), and H_2 (3) chemisorption at Pt-powder (173 K) vs. chemisorbed amounts [49].

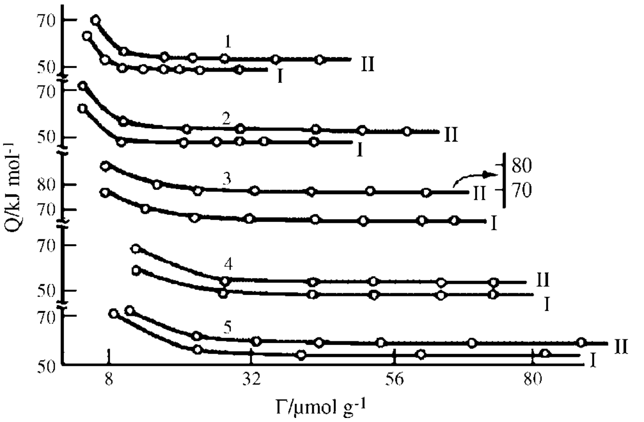

Fig. 13. Chemisorption of C_2H_4 (I) and C_3H_8 (II) at Co/Mg/Mo (1), Ni/Mg/Mo (2), Cu/Al_2O_3 (3), Ti (4), and Ag (5) oxides [67].

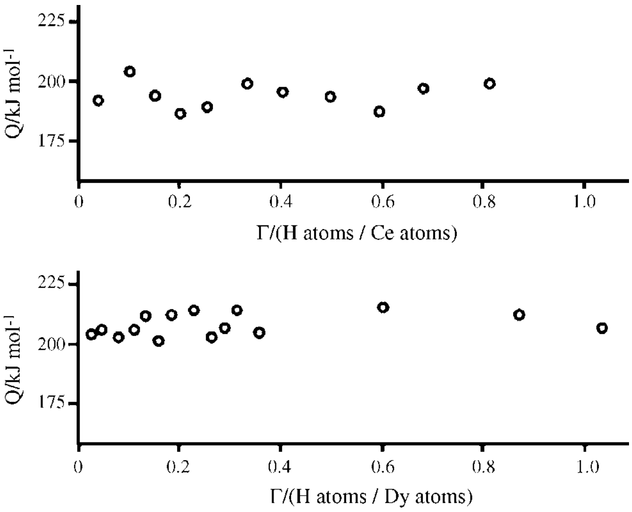

Fig. 14. Molar heats of H_2 chemisorption by lanthanides vs. relative H-content (295 K) [50].

alyst (see the table), and Pt-powder (Fig. 12) are homogeneous relative to H_2 CHS. Several other works demonstrating coverage-independence of molar heats of H_2 CHS at metals over wide ranges of surface coverages are listed at the end of Section 2.1.

In addition, we will consider H_2 CHS and sorption by Ce, Dy, Lu, Er, Tm, and Yb [50]. Fig. 14 shows the heats of H_2 CHS and sorption by Ce and Dy. The character of the data obtained for other rare-earth metals is similar. The molar heat effect does not vary with the H/M (M is a metal) atomic ratio. These results are of special interest for the theory of catalysis.

To explain the NH_3-synthesis kinetics that follows from the works by Winter [27] and Benton [26], Temkin assumed [25] that the surfaces of $Fe/K_2O/Al_2O_3$ catalysts and of a number of other catalysts are linearly heterogeneous. Factually, this hypothesis includes the assumption that the CHS heats decrease linearly with the surface coverage. Meanwhile, nobody proved experimentally surface heterogeneity of catalysts working in stationary catalytic processes. Even if the catalyzing surfaces were heterogeneous relative to the heats of CHS and relative to the reaction ability of their centers, there would be no physical grounds for surface heterogeneity to be linear. To explain the possibility of the uniform surface heterogeneity, it was taken that the surface electrons are as if located in an infinitely deep potential well giving a “surface electron gas” and that CHS influences the electron concentration and the kinetic energy of the near-surface electron layer and thus decreases the molar heats of CHS with the coverage; this assumption supplemented with several other hypotheses led to an equation giving linear decreasing in the heats of CHS with the surface coverage [89]. This concept was criticized in [32,90–95]. In particular, it was noted that, if the assumption on the surface electron gas were correct, the heat of H_2 dissolution in metals would be coverage-dependent as a result of a similar effect of the three-dimensional gas. The authors of [93,94] presented some examples when the heat of H_2 sorption was found to be constant.

The extensive measurements performed in [50] with many metals did not confirm the occurrence of coverage dependence in the heats of H_2 dissolution and, thus, refuted the hypothesis proposed in [89].

3. Sorption of reactants as an important factor influencing chemisorption and calorimetric studies

The data presented in this section relate to the sorption processes proceeding during the CHS experiments and between them.

The first example demonstrates H_2 sorption in the course of experiments on H_2 CHS at $Fe/K_2O/Al_2O_3$ catalysts of the NH_3 synthesis. The series of portion-by-portion experiments on H_2 CHS (Fig. 15, solid lines) were alternated with the experiments on portion-by-portion H_2 desorption (Fig. 15, dotted lines). The experiments were performed at 418 and 463 K. The desorption experiments were performed with no rise in the temperature through successive joining of the catalyst volume to a number of degassed volumes of the vacuum apparatus. In each of the series, CHS was partially irreversible, and, from series to series, hydrogen accumulated in the sample (Fig. 15b); the maximum amount of chemisorbed H_2 in these experiments corresponded to no more than 0.1 of the monolayer. For each chemisorbed and desorbed portion, the molar heat effects were measured (in Fig. 15a, the heats of desorption are given with the opposite sign). In Fig. 15b, each CHS curve was measured top-down and each desorption curve was measured bottom-up. In each of the four CHS series, the molar heats of CHS decreased as CHS proceeded. The hydrogen content in the sample after any regular desorption series was higher than that after the preceding desorption series. After each of four desorption series, the heats of CHS flied up almost to the heat of CHS

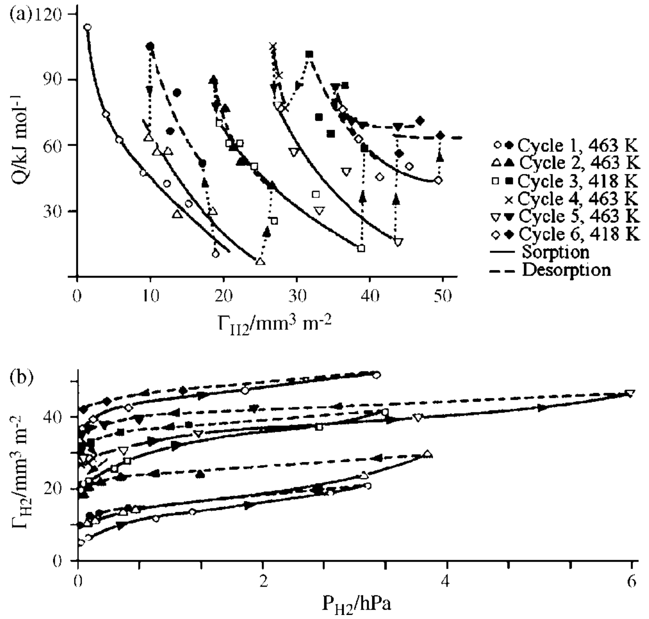

Fig. 15. Study of H_2 sorption by $Fe/K_2O/Al_2O_3/CaO$ catalyst in consecutive sorption–desorption cycles: (a) molar heats of sorption (solid curves) and desorption (dashed curves) vs. total sorbed amount (pointed lines with arrows show the sequence of the experimental series; (b) sorbed amount vs. H_2 pressure at the end of sorption (solid curves) and desorption (dashed curves) experiments; the arrows show the sequence of the experiments.

in the first experiment of the first series. Only in the fifth CHS series, the molar heat was almost coverage-independent. In the fifth desorption series, the measured molar heat became coverage-independent within the experimental errors. The thermodynamic analysis [11,77,96] of this phenomenon led to the following conclusions. During the first-fourth chemisorption–desorption series, the continuous saturation of the iron subsurface layers occurred. After termination of this process, surface CHS occurred. It is important that the molar heats of CHS in the fifth series were rather close to those obtained in [41] for H_2 CHS at Fe-films (see above, Fig. 4), in spite of the differences in the forms of the samples, experimental conditions, and techniques and procedures. It is clear that the performance of only one series of CHS measurements at the samples freed preferably of hydrogen could not reveal the surface–body diffusion. Such experiments would lead to the mistaken conclusion that, at 400–500 K, the H_2 CHS heats decrease with the coverage and that the surface is heterogeneous.

The experiments of Fig. 15 allow unambiguous revealing of the phenomenon of hydrogen sorption into the body of the catalyst. The above-given consideration shows that the data presented in Fig. 15 do not contradict the concept of surface homogeneity of the $Fe/K_2O/Al_2O_3/CaO$ catalyst, although the measured molar heat of H_2 CHS in the first series of the CHS experiments decreases with the coverage. However, such a way of proving the homogeneity is not optimum and the results presented in Fig. 4 (Section 2.2) and numerous results presented in Section 2.3 represent more demonstrative proofs of surface homogeneity for different iron surfaces. The example given in Fig. 15 shows that sorption of gases into the sample body can mask homogeneity of the surfaces of catalysts and chemadsorbents and lead to erroneous conclusions on surface heterogeneity. Room-temperature experiments with chemically pure and thermally degassed iron, apparently, allow obtaining correct conclusion on surface homogeneity, because the process of hydrogen diffusion into the iron body is activated (is characterized by activation energy) and proceeds at room temperature rather slowly, although the lower the temperature the higher the equilibrium sorption. However, the possibility of H_2 sorption in CHS experiments at heightened temperatures should be taken into account.

Sorption of gases into the bodies of thermally degassed catalysts and adsorbents represents a rather typical phenomenon. The processes of O_2 and H_2 sorption are characteristic for Cu- and CuO-containing systems, respectively.

As was said in Section 2.3, metal copper and the $Cu_4(OH_2)$-component of the $ZnO/Cu_4(OH_2)/Al_2O_3$ catalyst sorb O_2 [10].

Sorption processes are characteristic for different oxides. It was found that H_2 sorbs during the process of slow reduction of the CuO, CuO/Cr_2O_3 spinel, and $ZnO/CuO/Al_2O_3$ catalysts [10,78–80]. In these systems, hydrogen sorption is very significant and, in the case of the $ZnO/CuO/Al_2O_3$ system, can lead to $Cu_4(OH_2)$ formation with evolution of the corresponding amount of water [10,55]. It was recently shown that H_2 CHS at Cr_2O_3 is accompanied with diffusion of a portion of chemisorbed hydrogen into the solid body; Cr_2O_3 samples containing sorbed hydrogen are capable of sorbing additional amounts of oxygen as compared with its amount characteristic for completely oxidized oxides containing no hydrogen [12,97,98].

Sorption of gases by honeycomb oxide structures similar to zeolites represents a special problem. We dwell upon zeolite–adsorbate systems, which are being studied rather widely. Dependences of the molar heat on the sorbed amount are usually transmitted by drooping curves containing several small ledges, although coverage-independent molar heats are also available (i.e., pyridine adsorption by NaH-modernite [99] and n-hexane adsorption at zeolites containing different metals [100]). However, these dropping curves by no means signify that the zeolite surfaces are heterogeneous. This statement is based on two incontestable facts. First, ideal zeolites have no surface, and second, adsorption by ideal zeolites is not monolayer. It is well known that the ideal zeolite structure consists of small and large cavities. The small cavities are capable of housing one or two gas molecules; therewith, each sorbed molecule is circled by several different zeolite atoms and interacts simultaneously with all of them. The large cavities are capable of housing two or three layers of gas molecules, and the forces binding each of the sorbed layers to the zeolite structure and to the nearest sorbed layer are different not only in their values but even in their physical and chemical natures. The ledges in the dependences of the molar heats of chemisorption on the sorbed amounts reflect the occurrence of different modes of binding, and the drooping segments of these dependences are, apparently, nothing but transition curves. These transition curves reflect the fact that different modes of sorption can not be resolved due to slowness of diffusion processes and to smallness of differences between the binding energies inherent in different modes of sorption. This situation has next to nothing with monolayer chemisorption at metals or semi-conductors.

The processes of sorption can mask homogeneity of surfaces. This possibility was noted by Beeck more than 50 years ago [17]. However, even in our time, sorption processes are not always taken into account when chemisorption data are discussed.

4. Concluding remarks

Surface homogeneity is a fundamental feature of porous metals subjected to thermal stabilization and functioning under conditions of stationary catalysis or adsorption equilibriums. This statement relates to powders, films, wires, etc. We showed above that many researchers arrived at such a conclusion on the basis of calorimetric, thermodesorption, and isosteric studies of tens adsorbent–adsorbate systems. There is no ground to take that any metal catalyst shows itself as heterogeneous.

The problem of surface "homogeneity" vs. "heterogeneity" is usually considered as applied to the stationary catalysis and CHS equilibriums with the aim to clarify the nature of catalysis and to develop the best descriptions of the CHS equilibriums and of the rates of catalytic processes. Meanwhile, under stationary conditions, catalysts (and not only their surfaces) are affected by multi-component gaseous (or liquid) mixtures and, in the general case, chemisorb and sorb molecules, atoms, or radicals of different chemical compositions. Therefore, CHS of any individual gas at a catalyst freed preliminary of all chemisorbed and sorbed substances is not always equivalent to the CHS of this gas in the course of a catalytic process. It is clear that the proofs of surface homogeneity obtained at surfaces approached to their states occurring in the course of catalytic processes are most reliable for the theory and practice of catalysis. The data of this review show that similar heats of CHS are obtained for a number of thermally stabilized metal/adsorbate systems (i.e., Cu/O_2, Co/O_2, Ag/O_2, and Fe/H_2) independently of the form of metal (powder or film). However, the nonequivalence of the conditions at which the heats of CHS are measured at powders and films of the same chemical nature can lead to seeming differences, understanding of which can require an additional more detailed study.

For example, at the $Fe/K_2O/Al_2O_3$ catalyst approached to its state occurring in the course of NH_3 synthesis and containing sorbed hydrogen and chemisorbed nitrogen, H_2 chemisorbs at iron in the form of nitrogen/hydrogen radicals only (see Section 2.3 and [11,13,32,76,77]). However, the same catalyst subjected to the additional thermo-vacuum treatment and thus freed of sorbed hydrogen and chemisorbed nitrogen is capable of chemisorbing H_2 and of sorbing it into the Fe-body. In this case, CHS and sorption proceed simultaneously when a Fe catalyst contacts with H_2, the processes proceeding with different molar heat effects. If H_2 is dozed to the volume with a Fe-catalyst portion by portion, the ratio between chemisorbed and sorbed hydrogen varies from portion to portion and, therefore, the measurable molar heat effect changes from experiment to experiment.

Some researchers believe that certain of surfaces are homogeneous and the rest ones are heterogeneous relative to their catalytic and CHS characteristics under stationary conditions. Meanwhile, there is no reliable confirmation for such a position with respect to catalysts or adsorbents of specified chemical compositions located in any medium where a stationary catalytic or CHS process proceeds. Extended data obtained in [101] showed that catalytic reactions are capable of transforming crystal faces, decreasing their crystal indexes, and making them randomly distributed. In other words, in stationary states, the conditions of any catalytic reaction dictate some equilibrium arrangement to the surface CHS centers. It in no way follows that such surfaces reveal themselves as heterogeneous relative to the reaction ability of their active centers. This review shows that the critical consideration of data on the molar heats of CHS shows that surfaces are homogeneous.

Surface homogeneity manifests itself in the applicability of Boreskov's rule [102] to different catalyst–reaction systems. This rule states that the specific catalytic activity characteristic for catalysts of any definite chemical composition under any specified stationary conditions is almost constant for any catalytic reaction independently of the form of the catalyst (powders, supported materials, films, wires, etc.) and of the modes of their preparation and preliminary treatment. This rule works if the catalyst crystal size exceeds 3–5 nm (i.e., if the number of surface atoms in the catalyst is much greater than the number of body atoms in it). For example, it is stated that, neither for H_2 oxidation nor for SO_2 oxidation, the specific catalytic activity of Pt catalysts in the forms of SiO_2-deposited, black, wire, foil, and grid depends on the form of the catalyst, although the Pt specific surface of different catalysts varies by a factor of 4.35×10^4 [102]. Such a result can be observed either if the surfaces are homogeneous or if the character of heterogeneity of all the catalysts under consideration is the same; however, the last situation is unlikely for so different systems as black, wire, grid, etc. Thus, Boreskov's rule and the constancy of the molar heat effects observed in different adsorbent–adsorbate systems over wide ranges of surface coverages are manifestations of the same phenomenon of homogeneity of stabilized metal surfaces. (Boreskov showed that this rule relates also to different oxide catalysts.)

A number of studies of isotopic exchange also led to the conclusion on homogeneity of surfaces. In [103], such a conclusion was made on the basis of exchange between gaseous O_2 and oxygen chemisorbed at Ag powders. The studies performed by the differential isotopic method and based on the use of H_2, N_2, and their isotopes showed that all active centers formed by the surface atoms of crystal faces of porous platinum and graphite have the same CHS activity with respect to each of the studied gases, i.e., the surfaces of these adsorbents and catalysts are homogeneous relative to their reaction ability [104,105].

We do not consider the special features of very fine crystals. The available information on such crystals is insufficient for formulation of any solid conclusions on their CHS and catalytic characteristics. For the 3–5-nm crystals, the numbers of the surface and body atoms are comparable and the chemical potential of the surface atoms can be dependent on the crystal size. The unconventional CHS features of very fine crystals represent a special item. Synthesizing of such crystals of any preset size is a complicated problem. The affirmation that so fine crystals deposited on support materials are capable of being non-sintered during stationary catalytic processes proceeding at rather high temperatures and that they could be not speeded away by reacting gases for a rather long time under real conditions would be premature.

Therefore, we believe that, in the beginning, it would be useful to reach a consensus regarding the less complicated generally-valid problem on the homogeneity of active surface centers of usual catalysts working under stationary conditions and, thereafter, as new information becomes available, to attack more complicated problems.

The list given at the end of Section 2.1 shows that there are several tens of the systems for which the constancy of the molar heats of CHS is found over wide ranges of surface coverages; for a number of these systems, the results are confirmed by independent measurements performed in different laboratories. The analysis of calorimetric (and not only calorimetric) data presented in the review demonstrates the coverage-independence of the heats of CHS for metal powders, supported metal catalysts, specified components of multi-component catalysts, and evaporated films; from this analysis, it follows that the better are the adsorption and calorimetric techniques and procedures, the closer to zero is the angle between the heat–coverage function and the abscissa. Apparently, the conclusion on surface homogeneity of thermally stabilized catalysts and chemisorbents is the main general conclusion made on the basis of the semi-centennial studies of the heats of CHS of gases at metals.

No formalism is capable of proving surface heterogeneity. Meanwhile, in spite of numerous attempts to reveal surfaces satisfying the conditions of Kiperman's definition of heterogeneous surfaces, no such a surface was revealed in experimental studies performed over the 80-year period. The notion on heterogeneity of thermally stabilized surfaces has long since passed from the field of science to the field of faith. It exists owing to experimental imperfections in the measurements of the heats of CHS and to the hope that, one day, somebody will measure the coverage-dependent CHS heats and rates in the same work and will find that these two dependencies obey the regulations that wander from one textbook to another with no experimental confirmation.

For this 80-year period, the discussions even do not approach tightly to the hypothesis of surface heterogeneity in its formulation given above. To confirm this hypothesis, it is necessary to prove that, for any chemadsorbent–chemadsorbate system, the function that describes the decrease in the molar heats of CHS with the surface coverage and the function that describes the decrease in the reaction ability of the chemisorbed molecules or atoms with the surface coverage are interdependent in a definite manner. However, up to now, there is no work that would prove at least that the molar heat of CHS cleaned of side heat effects decreases with the surface coverage by any chemadsorbate in any definite manner over a wide range of surface coverage.

I accentuate that it is not a question of structural heterogeneity. There is no question about structural heterogeneity of the real catalysts and chemisorbents and even of foils, wires and films at which a stationary catalytic process proceeds. There is question of a hypothetical energetic heterogeneity in Kiperman's and Temkin's terminology that supposedly imparts different chemical activity to different surface centers. We stated that there are no reliable confirmations to this supposed phenomenon. The thermally stabilized surfaces reveal themselves as the homogeneous ones, i.e., any catalyzing metal surface works bodily, altogether. This our statement means that the notion on surface homogeneity is quite sufficient for explanation and analytical (mathematical) description of the stationary kinetics of heterogeneous catalytic reactions, equilibriums and rates of CHS, and rates of the isotopic exchange between gaseous and chemisorbed molecules. No mathematical description is capable of proving neither homogeneity nor heterogeneity of the surfaces. However, on the one hand, there is no reliable visualization, for understanding and description of which the notion on energetic heterogeneity of thermally stabilized surfaces would be necessary, and, on the other hand, one of the axioms of the natural sciences says that there is the ground to consider any phenomenon only under conditions that its reliable visualizations are known or (and) its occurrence follows from any fundamental scientific principles or from correct calculations based on fundamental principles. But there are neither fundamental principles nor fundamental calculations predicting surface heterogeneity. Moreover, we cited a number of experienced physicists and chemists who refused the possibility of a significant surface heterogeneity on the basis of common notions on the band theory of solids and on the basis of the calculations performed on the basis of this theory. According to the widely accepted Newton's statement, there are no grounds to devise a complicate explanation for the phenomena for explanation of which a simpler explanation is sufficient. The surface heterogeneity is taken as an entity; most of calorimetrists believe that it is proved by catalytists, most of catalytists believe that it is proved by calorimetrists, and most of theorists believe that it is proved by catalytists and calorimetrists, but, in reality, it is proved by nobody.

The history of the "homogeneity" vs. "heterogeneity" problem is considered in the brilliant review by S.W. Weller [106] and in my paper [32], and, today, I have nothing to add to these considerations.

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