Some problems in adsorption and calorimetric studies of the steps of catalytic processes

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Abstract: Principal side factors as well as technical and procedural peculiarities capable of distorting the results of measurements of adsorbed and desorbed amounts, of falsifying the nature of the processes proceeding in the systems under study, and of promoting artifacts in calorimetric and other studies of gas chemisorption on powders are considered. Modified techniques and procedures allowing the elimination of sources of side phenomena and artifacts and freeing traditional glass static adsorption apparatuses and experimental procedures from undesirable factors and peculiarities are proposed. Some available chemisorption and calorimetric data representing artifacts and also some data that are not artifacts but, due to imperfections of chemisorption techniques, show up as artifacts are presented and discussed. Several applications of the improved techniques and procedures to calorimetric and adsorption studies of the steps of catalytic processes proceeding on the basis of natural gas and of products of its processing are presented and discussed.

Key words: adsorption techniques and procedures, adsorption and calorimetric artifacts, calorimetric and chemisorption techniques, chemisorption heats, catalytic mechanisms, chemisorption mechanisms, heats of adsorption.

1. Introduction

This paper focuses on three aspects. First, it isolates a number of technical and procedural problems, artifacts, and side effects arising in the course of adsorption and calorimetric studies of catalyst states and mechanisms of heterogeneous catalytic processes (syntheses of CH_3OH, NH_3, and HCOH, shift-reaction, etc), mainly based on source substances (CO, CO_2, and H_2) produced from natural gas. Second, it describes means as well as technical and procedural approaches that allow elimination of or accounting for the side effects and preventing the artifacts. Third, it demonstrates several applications of the improved techniques and procedures for solving different scientific problems in heterogeneous catalysis.

Most of the technical problems that should be solved in each adsorption or desorption experiment are dictated by side processes that are difficult to identify and control. The correctness of the measurements of the adsorbed or desorbed amount depends not only on the skill of the experimenters, but also on the current state-of-art of the adsorption techniques. Available microcalorimeters meant for studying the heat effects of chemisorption processes proceeding at constant temperatures (for example, the families of Tian-Calvet [1,2] and FOSKA [3] calorimeters) are capable of measuring the heats of adsorption on powders when the powder amount in each experiment is 10-100 μmol or more, and are capa-
ble of recording thermokinetic curves for any length of time [3]. The thermokinetic curves also represent unique, highly sensitive and precise tools for revealing the heat effects not directly associated with adsorption or desorption, for example, the heat effects of postadsorption, postdesorption, and other side processes [2]. Thus, it is possible to reveal the processes noncoverable in studies based on traditional volumetric methods. Meanwhile, the correct measuring of the heats of adsorption or desorption of small amounts of gases is a rather complicated problem. It is evident that the heat effects should be related to the amount of the individual substances reacting in a strictly determined process. However, techniques and procedures intended for adsorption measurements at elevated temperatures can initiate side effects of different origins. On frequent occasions, the side effects significantly influence the results of chemisorption or heat measurements, and can be the cause of erroneous experimental results. The causes of irreproducibility of adsorption and calorimetric data are not perceived in full measure in the literature. This paper represents a generalization of the available experience in the clearing of side effects from results of chemisorption measurements and, in particular, from calorimetric studies of chemisorption. It is based on our activities started in the early 1960s [4,5]. Some specific approaches for the measurement of heat effects accompanying physical adsorption are considered, for example in [6,7].

During chemisorption, the following side processes are most frequent: interaction of the adsorbate with substances previously adsorbed and formation of adsorbed or gaseous products; interaction of the adsorbed grease vapor with the adsorbent; diffusion of the adsorbate into the solid body; interaction of the adsorbate with impurities or with solid components diffusing from the body to the surface; adsorption of the adsorbate on the walls of the adsorption apparatus; and chemical interaction between the adsorbate and the walls of the adsorption apparatus, metal taps, balances, and so on. In the course of adsorption experiments, each of these processes may influence the values of the heat effects measured, the gas amounts actually adsorbed or desorbed, and the surface-body distribution of the adsorbate in the solid. Therefore, it is necessary to preclude or take into account all these side phenomena. Revealing and quantitative measuring the side phenomena are principal directions of technical and procedural progress in studies of gas-solid processes.

Getting rid of the side contributions from the heat effects and adsorbed or desorbed gas amounts is a combined physical-chemical and calorimetric problem. Sometimes, it is possible to preclude all side processes and thus to measure the heat effects initiated solely by the processes under study. Otherwise, it is necessary to isolate each of the side processes and to measure their molar or specific heat effects. For the adsorbate amount to be correctly determined, it is necessary to preclude or to take into account the surface-body diffusion of the adsorbate, its interaction with the impurities distributed within the powder, and the desorption of the products of this interaction. It is reasonable that these processes should be controlled not only in the course of the adsorption-desorption experiments, but also between them, in order to specify the adsorbent state before each experiment. Inspection of the grease-vapor effect (in apparatuses with greased taps), gas adsorption-desorption at the apparatus walls, and body-surface diffusion of impurities in the sample are also necessary.

In each epoch, the scientific notions on natural processes and phenomena are the result of deflection of actual regularities through the prism of common perceptions changing in time. Therefore, it would appear reasonable that, from time to time, the results of some experimental measurements should be revised. It would be misjudging to consider such a revision as a defamation of earlier scientific work. Actually, it is a natural consequence of the accretion of knowledge and development of experimental possibilities. Apparently, the progress in traditional techniques and procedures should be demonstrated in the literature in order to avoid in future the defects of earlier work and to explain the differences between the results of measurements separated in time.

It goes without saying that each investigator seeks to eliminate side processes. However, not each one manages to do it, since it does not always happen that all side processes accompanying adsorption are identified and are studied adequately relative to their dependences on different parameters. The aim of this paper is not a criticism. The paper deals with errors of the epoch rather than of the individuals (saeculi vitia, non hominis). The aims of the paper are to assist active investigators to extract correct information from the available literature and to prevent technical errors in the future.
2. Technical and procedural features responsible for adverse effects and artifacts in chemisorption studies; improved instrumentation and procedures

2.1. Hydrocarbon grease as a source of experimental errors and artifacts

At present, hydrocarbon compositions are being not uncommonly used to grease taps of vacuum apparatuses intended for studies of gas adsorption on powders. Furthermore, when results obtained previously at elevated temperatures are used or discussed, it is of importance to understand the nature of the adverse effect of hydrocarbon grease on the adsorption results. Meanwhile, although it is well known that any contact between the adsorbents and the grease vapors is unwanted, no work, other than almost unavailable work [8], has contained consideration of the nature of adverse grease effect on the results of adsorption studies.

The equilibrium pressures of hydrocarbon greases are very low. Therefore, the degree of coverage of the pure metal surfaces by the grease vapor at room temperatures and, all the more so, at elevated temperatures, is negligible. However, it is necessary to take into account the following processes proceeding at partially oxidized surfaces of metals (Me) and oxides (MeO), such as CuO, NiO, etc., at room temperatures during night and weekend intervals between experiments:

\[ \text{MeO} + C_n \text{H}_{2n+2} = \text{MeO}[C_n \text{H}_{2n+2}]_{\text{ads}} \] (1)

\[ \text{MeO}[C_n \text{H}_{2n+2}]_{\text{ads}} + 4n\text{MeO} = (4n + 1)\text{Me} \cdot n[\text{CO}_2]_{\text{ads}} \cdot (n + 1)[\text{H}_2\text{O}]_{\text{ads}} \] (2)

In the course of experiments, the adsorbent is usually protected against grease vapors by a trap cooled to 77 K, but the trap temperature can rise in the course of prolonged intervals between experiments. As a result of reaction (2), carbonate and water steadily cover the surface. In the course of heating of the sample immediately before the experiments, CO\(_2\) and H\(_2\)O can be desorbed; in this case, the surface is being reduced, i.e., its coverage with oxygen is being decreased.

\[ (4n+1)\text{Me} \cdot n[\text{CO}_3]_{\text{ads}} \cdot (n+1)[\text{H}_2\text{O}]_{\text{ads}} = \\
(3n+1)\text{Me} + n\text{CO}_2 + (n+1)\text{H}_2\text{O} + n\text{MeO} \] (3)

Sometimes, CO\(_2\) and H\(_2\)O are not desorbed completely before the experiments and are being desorbed in a cooled trap during the subsequent experiments on adsorption of O\(_2\), H\(_2\), or other gases. Neglect of the heat effect associated with the CO\(_2\) and H\(_2\)O desorption can significantly falsify the heat of adsorption under the measurements.

Therefore, hydrocarbon greases are undesirable. Nevertheless, if they are applied, the heat effects resulting from adsorption of O\(_2\), H\(_2\) and other gases should be corrected. Namely, it is necessary to measure the molar heats of adsorption(or desorption) of CO\(_2\) and H\(_2\)O, to analyze the CO\(_2\) and H\(_2\)O amounts in each adsorption experiment, and to take into account the side heat effect of CO\(_2\) and H\(_2\)O desorption in the course of adsorption of the gases under study. Besides, it is necessary to correct the oxygen amount at the adsorbent by taking into account the oxygen amount that has incorporated into the CO\(_2\) and H\(_2\)O desorbed from the surface. Our experience shows that these corrections may be rather significant.

2.2. Standardization of the samples under study

The standard state of a metal or oxide sample is its reproducible chemical state achievable as a result of technically specified thermo-vacuum cleaning (and the subsequent oxidation if the sample represents a metal oxide) provided by body-to-surface diffusion and subsequent desorption of all foreign elements transformable to volatile substances. For the standard states thus obtained, we take that the contents of H, C, O, and other foreign elements in metal samples and of H, C, excessive O, and other foreign elements in oxide samples are equal to zero.

Standardization of the state of adsorbents before adsorption studies is an old problem. On frequent occasions, each investigator solves it in an individual manner, and such a situation impedes correlation of sister data obtained in different laboratories and, sometimes, the data obtained with different samples in the same laboratory. This problem is of particular importance when adsorption of two gases interacting with one another in adsorbed states is under study. Meanwhile, such experiments are useful for understanding of the mechanisms of catalytic processes. When applied to metals or oxides (or other two-element adsorbents, such as sulfides etc.), this problem has specific peculiarities. We try to evaluate quantitatively the grade of solution of the problem.
of standardization of powder adsorbents and to propose simple and sensitive techniques and procedures applicable for this aim.

The content of the problem is as follows. Very often, porous solid adsorbents and catalysts contain “biographical” impurities such as water and carbon. The former can be introduced from the mother solutions or from the atmosphere. The latter can be introduced from source carbonates or added in the form of graphite to improve the process of tableting. Sometimes, samples contain nitrates. During the thermal pretreatment before the experiments and in the course of them, water and carbon diffuse to the surface and react with the adsorbed particles. Sometimes, the products of surface reactions desorb from the samples into the volume of the adsorption apparatuses and precipitate in the cooled traps. These side processes can change the observable adsorption capacity of the samples and induce additional heat effects. Besides, the occurrence of unknown amounts of water (or OH groups) and carbon in the samples before the experiments causes an uncertainty in the elemental composition of the samples in the course of the experiments. Usually, experimenters heat the samples under vacuum before the adsorption studies to free them of water and carbon. Such a pretreatment takes much time because it should be performed at a rather low temperature to provoke minimum sintering of the samples under study. As a rule, the pretreatment being performed under static conditions can not be intensified by vacuumization because the rate is limited by intracrystalline diffusion and, sometimes, by product diffusion from the porous structure into the apparatus volume. For standardization, the oxide samples should be re-oxidized after their thermo-vacuum pretreatments.

The degree of cleaning and the amounts of all side substances desorbed during the adsorption experiments should be controlled quantitatively. This control is necessary for experimental data on adsorption and adsorption heats to be reproducible and uniquely interpretable. The techniques and procedures allowing the provision of these requirements are presented below. They are also applicable to the measurements of the characteristics of simultaneous adsorption of two adsorbates interacting with one another in the adsorbed layer.

Examples of standardization performed by thermo-vacuum pretreatment of the samples of an industrial CuO/ZnO/Al$_2$O$_3$ catalyst [9] (SNM-1 [10]), an Ag catalyst [11] (both prepared from carbonates), and an Au catalyst [12] (reduced from precipitated auric hydroxide obtained on the basis of “analytically pure” auric chloride acid and Na$_2$CO$_3$, as in [13]) are given in Figure 1, Table 1, and Table 2, respectively. These examples will show that the standardizing pretreatments should be more prolonged and intensive than those performed in many available studies. In the following sections of this paper, we will try to show the effectiveness of the intensive standardization for the clarification of different details of the adsorption mechanisms.

From Table 1, it can be seen that prolonged treatment by H$_2$ flowing through the sample at 623-653 K and degassing at 613-653 K are necessary for

<table>
<thead>
<tr>
<th>N</th>
<th>Operation</th>
<th>Temperature (K)</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>reduction in H$_2$ flow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>oxidation by O$_2$</td>
<td>stepwise rise from 373 to 633</td>
<td>633</td>
</tr>
<tr>
<td>3</td>
<td>thermo-vacuum treatment (with a trap cooled to 77 K)</td>
<td>633</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>repeated reduction in H$_2$</td>
<td>523</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>573</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>653</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>degassing at $10^{-4}$ Pa</td>
<td>573</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>653</td>
<td>4*</td>
</tr>
<tr>
<td>6</td>
<td>final reduction in H$_2$</td>
<td>623-633</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>degassing at $10^{-4}$ Pa</td>
<td>593-613</td>
<td>10**</td>
</tr>
</tbody>
</table>

The specific surface area after pretreatment is 0.15 m$^2$/g.

* After this operation, the desorption of CO$_2$ terminates and the desorption of H$_2$O falls down to 1.5 $\mu$g/(g-h).

** No H$_2$O desorbs (the limit of detection is 0.2 $\mu$g/(g-h)).
Ag reduction as well as for the cleaning of CO$_2$ and H$_2$O from the metal. This procedure for the reduction of Ag is much like that used in [14]. However, it is significantly more intensive than the pretreatments performed in a number of other studies of the powder silver-oxygen system.

Figure 1 gives the standardization protocol and the mean rates ($r$) of thermo-vacuum desorption of CO$_2$ and H$_2$O from the CuO/ZnO/Al$_2$O$_3$ catalyst at different stages of its pretreatment. It can be seen that the processes of CO$_2$ and H$_2$O desorption terminate at 723 and 623 K, respectively. Total desorption exceeds the volume of one monolayer by a factor of several units. The pretreatment takes more than 100 h.

Table 2 lists the stages of the pretreatment of sample 2 of powdered Au catalyst used in [12] before studying O$_2$ and H$_2$ adsorption. Unlike the examples illustrated by Table 1 and Figure 1, this Au sample was pretreated in a glass apparatus with greased taps. This is an example of excessively intense pretreatment.

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Operation</th>
<th>$T$/K</th>
<th>$p$/hPa</th>
<th>Duration (h)</th>
<th>Final rate of H$_2$O desorption ($(\text{cm}^3 \text{ of H}_2\text{O vapor})/\text{(g·h)})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$, flow</td>
<td>318–523</td>
<td>26</td>
<td>300</td>
<td>8·10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>pumping</td>
<td>525</td>
<td>down to 10^{-6}</td>
<td>60</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>O$_2$</td>
<td>473</td>
<td>0.1</td>
<td>to saturation</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$</td>
<td>573</td>
<td>0.13–340</td>
<td>70</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>pumping</td>
<td>573</td>
<td>down to 10^{-6}</td>
<td>170</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>H$_2$</td>
<td>623</td>
<td>10.5</td>
<td>1</td>
<td>9·10^{-2}</td>
</tr>
<tr>
<td>7</td>
<td>pumping</td>
<td>623</td>
<td>down to 10^{-6}</td>
<td>250</td>
<td>4·10^{-3}</td>
</tr>
<tr>
<td>8</td>
<td>washing</td>
<td>323</td>
<td>by running flow of bidistilled H$_2$O</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>H$_2$</td>
<td>623</td>
<td>0.13–14</td>
<td>60</td>
<td>2·10^{-4} at $p$(H$_2$)=20 hPa</td>
</tr>
<tr>
<td>10</td>
<td>pumping</td>
<td>623</td>
<td>down to 10^{-6}</td>
<td>70</td>
<td>4·10^{-5}</td>
</tr>
</tbody>
</table>

The specific surface area after the adsorption experiments is 0.40 m$^2$/g.

It was expected that a certain amount of “biographical” NaOH and NaCl might exist on the sample surface after the thermo-vacuum pretreatment. The aim of the water washing was to clean sodium from the surface. The subsequent pretreatment was continued at 623 K and was terminated when the rate of water desorption was decreased to the limit of its detection, about 0.05% of one monolayer per hour. Apparently, the washing was unnecessary and the thermo-vacuum pretreatment at 573 K was sufficient, because sample 1 pretreated with no washing showed almost the same adsorption characteristics as sample 2 (the specific surface of sample 1 was 1.6 m$^2$/g, i.e., four times that of sample 2).

Beginning from the standard state, a long series of alternate adsorption and desorption experiments with different adsorbates can be performed at each powder sample with no contact with the atmosphere. The applied procedures allow us to know the current excesses in the O, H, and C elements over the standard state for any adsorbent under study. For metals, these excesses can be either positive or equal to zero. For oxides, the excessive oxygen content can be positive or negative. The negative excesses result, for example, from H$_2$ adsorption accompanied by H$_2$O desorption. These procedures allow not only the standardization
of the state of different samples of any one adsorbent before the first series of adsorption of a gas, but they also allow the measurement of the rates and heats of adsorption as well as the maximum adsorbed amounts as functions of the concentrations of several different adsorbed elements occurring in the adsorbents. For example, it is possible to measure the rates and heats of O₂ adsorption against the amount of oxygen adsorbed on the sample at different specified contents of hydrogen adsorbed previously. Measurements of such a kind are of great importance for clarification of the adsorption and catalytic mechanisms on surfaces containing adsorbed particles having different chemical elements.

2.3. Chemisorption accompanied by surface interaction and desorption

Problems of such a kind are multiform and have no common solution [8]. We will consider below some approaches allowing elimination of the effects introduced by the side desorption and surface interaction from the chemisorption characteristics under

\[ Q(H₂) = (q(H₂) + Q_{ads}(H₂O) \cdot n(H₂O) + Q_{ads}(CO₂) \cdot n(CO₂))/n(H₂) \]  
\[ Q(CO) = (q(CO) + Q_{ads}(H₂O) \cdot n(H₂O) + Q_{ads}(CO₂) \cdot n(CO₂))/n(CO) \]  
\[ Q(O₂) = (q(O₂) + Q_{ads}(H₂O) \cdot n(H₂O) + Q_{ads}(CO₂) \cdot n(CO₂))/n(O₂) \]

where \( q(H₂) \), \( q(CO) \), and \( q(O₂) \) are the heat effects measured in experiments on chemisorption of H₂, CO, and O₂, respectively; \( Q_{ads}(H₂O) \) and \( Q_{ads}(CO₂) \) are the molar heats of H₂O and CO₂ chemisorption measured in special experiments at a surface state close to that during the experiments on H₂, CO, and O₂ chemisorption; \( n(H₂O) \) and \( n(CO₂) \) are the molar portions of H₂O and CO₂ desorbed; and \( n(H₂O), n(CO), \) and \( n(O₂) \) are the molar portions of chemisorbed H₂, CO, and O₂.

As an example of chemisorption accompanied by desorption, we consider H₂ adsorption on Ag precovered with oxygen. Silver precovered with oxygen chemisorbs H₂ at elevated temperatures, although reduced Ag does not chemisorb H₂. Figure 2 [11] presents the molar heats of chemisorption of H₂ at Ag vs the surface H/O ratio.

In the course of each of the experiments on H₂ chemisorption, a portion of the hydrogen forms water vapor. This H₂O condenses in the cooled trap 5 located outside the calorimeter (Figure 3(a), see below). The heats of chemisorption of H₂ are computed by measurements. Suppose that the H₂, CO, or O₂ chemisorption heats or other characteristics of a pure or partially oxidized metal surface or an oxide surface should be measured. Assume that the surface under study contains C, H, and O preadsorbed or not cleaned in the course of pretreatment of the adsorbent. Gas adsorption on such a surface may be accompanied by desorption of surface substances, such as CO₂ and H₂O. Let the desorption be associated with a side heat effect and change the elemental composition of the adsorbent. Quantitative measurement of the CO₂ and H₂O volume desorbed in the total volume over the adsorbent can be hampered by the adsorption on the apparatus walls. Meanwhile, accurate analyses of the desorbed amounts of CO₂ and H₂O are necessary for careful measuring of the molar heats of adsorption of the gases under study, and for gaining of greater insight into the mechanisms of the surface processes.

To compute the molar heats of chemisorption of H₂, CO, or O₂ accompanied with some desorption of CO₂ and H₂O, the following equations are applicable:

![Figure 2. Heats of hydrogen adsorption on silver surface covered with oxygen versus H/O ratio at the surface: series I, 411–418 K (black circles), series II, 465 K (black squares), and series III, 356.5 K (light squares); The numerals indicate the consecutive order of the experiments; before experiment 1, the sample contained 0.24 cm³ (ntp) O₂/m²; the minimum oxygen content at the sample was 0.12 cm³ (ntp) O₂/m²; after experiments 22, 27, 31, and 33, measured oxygen amounts were adsorbed additionally.](image-url)
taking into account the process of $\text{H}_2\text{O}$ formation. This computation is possible because the water amount as well as the heats of chemisorption of the oxygen interacting with hydrogen at the same coverage and at the same surface $\text{O}/\text{H}$ ratio are measured in special experiments. In these computations, the tabulated value of the heat of $\text{H}_2\text{O}$ formation from the elements was applied. As can be seen, $\text{H}_2$ chemisorption proceeds up to $(\text{H}/\text{O})=1.8$.

![Diagram of improved glass apparatuses](image)

**Figure 3. Principal fragment of improved glass apparatuses intended for studies of chemisorption and desorption, including the heat effects of these processes**

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; 15—Glass tap

(a) Desirable design, (b) Admissible design, (c) Inadmissible design

### 2.4. Effect of walls of adsorption apparatuses

The glass and metal walls of adsorption apparatuses, including the metal taps and their grommets, balances, and other apparatus elements, are capable of adsorbing gas and vapor and, sometimes, can even react with them. These phenomena can influence significantly the results of adsorption measurements. In the course of different experiments, the metallic parts of the apparatuses contact with oxidizing or reducing gases. Such contacts can change the surface properties of the apparatuses. In the course of the adsorption experiments on catalysts, the following phenomena sometimes occur on the metal walls of the adsorption apparatuses: after contacting with $\text{O}_2$, the metal walls can gain ability of converting $\text{H}_2$ into OH chemisorbed on their surfaces and $\text{H}_2\text{O}$ vapor; after contacting with $\text{H}_2$, the metal walls can gain ability of chemisorbing $\text{O}_2$ or converting $\text{H}_2\text{O}$ vapor into chemisorbed OH and gaseous $\text{H}_2$ and the walls of the Ag-protected components of metal taps and other apparatus elements can gain ability of converting $\text{H}_2\text{S}$ into surface sulfide and gaseous $\text{H}_2$; etc.

The possibility of such effects should be considered for the measurements to be accurate. The instrumentation presented below allows the controlling of such phenomena.
2.5. Improved glass adsorption apparatuses and experimental procedures

Figure 3(a) presents the principal fragment of the improved glass apparatuses meant for studies of chemisorption, desorption, and heats of chemisorption of O$_2$, H$_2$, N$_2$, CO, HCOH, CO$_2$, H$_2$O, NH$_3$, CH$_2$OH, C$_n$H$_{2n+2}$, C$_n$H$_{2n}$, etc. on powdered catalysts and adsorbents. These apparatuses are based on volumetric methods of measurements. Some specific technical approaches meant for studies of individual steps of catalytic gas-solid heterogeneous polymerization processes, methanol synthesis from H$_2$ and carbon oxides, and water adsorption are described in [15], [9], and [16,17], respectively, and are not considered in this paper.

Each apparatus is supplied with a sample ampoule and a reference ampoule (Figure 3(a); 1 and 2, respectively). The ampoules are intended for studies of different adsorbent-adsorbate systems, as described in [3,8]. The sample ampoule contains the accurate weight of a catalyst or an adsorbent pretreated to achieve its standard state. During the pretreatment, the sample ampoule can be located inside or outside of the calorimeter (Figure 3(a)). If the latter mode is applied in a pretreatment, the pretreated ampoule is sealed under vacuum across the neck 12, housed in the calorimeter, and sealed to the A-A section of the glass apparatus. Then, the thin glass diaphragm 14 should be broken by the glass-covered magnetic cylinder 13 driven by an outer magnet. The reference ampoule is identical to the sample one, but it contains an inert solid material, e.g., small glass spheres. The glass apparatus fragment presented in Figure 3(a) is supplied with grease-free metal bellows taps connected to the glass through kovar insertions. The apparatus has two fundamental peculiarities. First, it includes two stainless-steel taps 3 and 4, divided from each other by the U-shape glass trap 5, which can be cooled by a refrigerant if it is required. This package and the following experimental procedures allow the precooling of any grease and mercury effects on the results of adsorption and heat measurements. Second, it contains the package 9-10-11, which has been carefully calibrated. This package (below, the device for analyses) allows an accurate measurement of the CO$_2$ and H$_2$O amounts in their mixtures in the range of 1–50 mm$^3$ ntp, and it can provide a sensitivity of 0.1 μmol if the manometer 11 and the trap 10 have diameters given in Figure 3(a) and a height of 60–70 mm.

Before the experiments, we degas the principal fragment of the apparatus (Figure 3(a)) to 10$^{-5}$ Pa by using a vacuum pump. From time to time, we perform repeated treatment of all glass tubes and details of the apparatus under vacuum by an outer marginal discharge induced by a 10–20 kV spark coil detector and heat the metal taps at about 423 K for about 25 h by using an outer wire electric heater. Such processing stimulates desorption from the walls of the apparatus into the evacuated space. It is stated that the walls of the apparatus thus treated adsorb the gases and vapors under study (including water) only slightly and the adsorbed molecules can be desorbed from the walls and frozen completely in a trap cooled to 77 K for 30–40 min.

We consider that this apparatus is applicable to adsorption and calorimetric experiments if the following conditions are fulfilled. First, the leakage into the isolated apparatus fragment with metal taps degassed down to 1·10$^{-4}$ Pa should be less than 0.1 Pa in 15 h. Second, the total H$_2$O and CO$_2$ amount condensable in 1 h in the trap 10 connected to the apparatus fragment shown in Figure 3(a) and cooled to 77 K should be below 0.05 μmol.

We calibrate the volume of each part of the apparatus with an accuracy of 1%. Each volume containing a trap is calibrated twice: with the trap kept at room temperature and with the trap dipped into a cooler to a fixed level. A rather small volume between the taps 3 and 4 is calibrated through computation on the basis of measurements of its geometric size. The other volumes are calibrated by using dry helium, Boyle’s law, the bulbs already calibrated, and the big mercury U-shape manometer located beyond the fragment shown in Figure 3(a). The glass tube of the big manometer has an inner diameter of 12 mm. This manometer allows the pressure to be measured up to 700 hPa.

We measure the pressure with Hg-manometers and by means of a cathetometer having an accuracy of 0.01 mm, with the thermocouple-gage tube 8 calibrated to an accuracy of 2%–4% by using individual gases, and with an ionization-gage tube not presented in Figure 3(a).

The device for analyses, located to the right of the tap 9, is intended for analyzing quantitatively very small amounts of completely vaporizable H$_2$O, CO$_2$, and their mixtures, as well as for analyzing CH$_3$OH, HCOH, HCOOH and some other vapors desorbed from the adsorbents and catalysts. To compute the amounts of the vapor substances, we use the vol-
ume values of the manometer tube and of the capillary trap 10. These values are determined previously, i.e., before soldering the device for analyses, by repeated extruding the weighed Hg-columns into the tubes and metering the lengths of the Hg-columns. We take into account the facts that the vapor amount in the device for analyses depends on the trap temperature (the vapor amount is not the same when the trap 10 is at room temperature, 77 K, or 195 K), and that the space of the device for analyses is pressure-dependent since the mercury level is moving. For example, the procedure for the analysis of (H$_2$O+CO$_2$) is as follows: the total (H$_2$O+CO$_2$) pressure is measured with the small Hg-manometer 11, the trap 10 is cooled down to 196 K by a mixture of alcohol and “dry ice”, and the CO$_2$ pressure is measured as before. Using the volume value and introducing the corrections for the trap temperature and the change in the Hg level at each pressure measurement, we compute the individual amounts of CO$_2$ and H$_2$O. To preclude H$_2$O condensation on the walls, the H$_2$O amount being analyzed should be so small that its pressure would not exceed (0.5−0.6) $p_0$ ($p_0$ is the saturation pressure). The volume of the device for analyses is limited by the specified sensitivity and usually ranges from 2.5 to 3.2 cm$^3$. We compute this volume with an accuracy of 0.001 cm$^3$. To minimize the volume of the device and to achieve a rather high accuracy in pressure measurements, we use a capillary of diameter 1.5 mm and a tube of diameter about 4.5 mm in designing the trap 10 and the manometer 11, respectively. The calibration of the elements of this device before their sealing all together is described above. The procedures of analyzing the mixtures containing CH$_3$OH, HCOH, and HCOOH vapors are described in [9] and are detailed in [18].

The apparatus has a small glass bulb with a Pt-wire that can be electrically heated (not given in Figure 3(a)). This device is used for complete combustion of H$_2$, CO, CH$_3$OH, HCOH, HCOOH, and their mixtures in an excess of oxygen. The combustion is a step of quantitative analyses of the products desorbed under vacuum from the catalysts.

To clarify the mode of operation with the apparatus under consideration, we schematically describe below the standard adsorption and desorption experiments.

The adsorption experiment can consist, for example, of the following operations: degassing the apparatus; dosing a well-specification amount of an experimental gas or vapor to the volume between the taps 4, 7, and 9; cooling the trap 5 to 77 K (or 196 K); connecting the volume of the ampoules 1 and 2 to the apparatus volume with a gas portion and monitoring the process under study through a thermokinetic curve and the manometer 8; isolating the volume of the ampoules 1 and 2; connecting the trap 10 to the trap 5; heating the trap 5 to room temperature; condensing the reaction products in the trap 10; isolating the device for analyses; and analyzing the products desorbed to the trap 5 in the course of the experiment. This analysis can be supplemented with burning of the products by using the bulb with the Pt-wire or by using other techniques described in [9] and by subsequent analysis of the combustion products by using the device for analyses (9-10-11).

Desorption experiments can be performed, for example, as follows: degassing the apparatus, with the exception of the volume with the ampoules 1 and 2, and isolating the fragment given in Figure 3(a); connecting the volume of the ampoules 1 and 2 to the volume between the taps 3 and 4 until the equilibrium is reached (monitoring on the basis of the thermokinetic curve); isolating the volume of the ampoules 1 and 2; and analyzing the gas of the volume between the taps 3 and 4 by using the device for analyses (9-10-11), the manometer 8, the bulb with the Pt-wire for burning, and the bulb with powdered Pd (see [9]) meant for H$_2$ adsorption.

Such techniques and procedures, in combination with the standardization of the initial state of the solid samples, allow rather accurate monitoring of the composition of the solid samples in the course of each experiment and prevent any effect of grease vapors on the experimental results.

Use of greased glass taps instead of metal taps results in serious measurement errors and fundamental artifacts (see below). For the apparatuses where the corresponding package is designed as that shown in Figure 3(b), the experimental results can be improved by paying special attention to the possible adverse effect of grease vapors and by conducting computational corrections. The use of the package shown in Figure 3(c) puts the results in doubt.

Each of the technical and procedural modernizations described above may appear to be insignificant. However, we will show below that these modernizations taken together allow refinement of the available notions on the actual mechanisms of catalytic and adsorption processes.
3. Artifacts, confusing measurements, and seeming artifacts clarified due to the technical and procedural modernizations

The history of studies of the catalytic and chemisorption phenomena provides a lot of examples of principal artifacts induced by imperfect measurements as well as theoretical developments based on these artifacts. Some of the artifacts and questionable theoretical developments had been originated in the midtwentieth century or earlier and migrated from one monograph to another, in spite of the fact that the measurements used as the basis were imperfect and were not reproduced by subsequent investigators.

3.1. Imperfection of experimental techniques as a cause of the notion that surface heterogeneity is of fundamental importance in catalytic and chemisorption processes

Recently, we have shown [19] that the assumptions of the principal effect of geometric and induced heterogeneities of metal surfaces on chemisorption and catalytic processes proceeding at them are not justified. This conclusion leans upon the following facts.

First, the notions of surface heterogeneity are inconsistent with several fundamental scientific conclusions. It is well known that the ability of catalyzing a definite chemical reaction is a particular feature of a very limited number of chemical substances, and the catalytic activities of unit surface areas of these substances in this reaction differ significantly. Thus, the catalytic action of any substance in any reaction is the specific feature of this substance. On the other hand, it is generally accepted that the catalytic activity (and selectivity) of a solid in any reaction is determined by the possibility of formation of definite surface intermediates and that these intermediates can be formed on those surface centers which are characterized by a suitable energy of bonding of the source reactants, i.e., by a suitable heat of chemisorption. However, if such surfaces on which the heats of chemisorption of source reactants are highly dependent on the coverage would exist, the surface intermediates suitable for different reactions would be formed on them and the understanding of the phenomenon of the catalytic action specificity would be hampered. In addition, it is difficult, if at all possible, to bring the notion that surface heterogeneity is of importance for the catalytic and chemisorption processes into coincidence with the following two fundamental conclusions made by Boreskov: (1) The specific catalytic activity of films, wires, filaments, powders, and supported metals (with crystal sizes larger than 3–5 nm) which are chemically identical but produced on the basis of radically different methods is approximately the same. (2) Under the influence of reacting gaseous mixtures, the surface layers of catalysts rearrange themselves and the states of the surface layers, which are either equilibrium or quasi-equilibrium relative to the reacting mixtures, are formed. In other words, catalyst surfaces are influenced by reacting gaseous mixtures and are transformed by them [20].

Second, the so-called logarithmic isotherms deduced from notions on surface heterogeneity are applicable [19,21] for the description of chemisorption on homogeneous surfaces if each molecule adsorbs at several surface centers; therefore the applicability of these isotherms do not prove that the surfaces are heterogeneous.

Third, the so-called Elovich equation (the same as the Zeldovich-Roginskii equation) giving the exponential relation between the chemisorption rate and the surface coverage is applicable to the description of chemisorption on homogeneous surfaces if each molecule adsorbs at several centers; therefore its applicability does not prove that the surfaces are heterogeneous [19,21].

Fourth, the power-law kinetic equations obtained earlier [22,23] from notions on surface heterogeneity and confirmed by measurements of reaction rates in reacting gas mixtures of different compositions can also be deduced for homogeneous surfaces. This problem was considered in [19,24] by the examples of catalytic reactions of NH$_3$ synthesis on promoted Fe-catalysts, SO$_3$ synthesis on Pt, H$_2$ and CO$_2$ formation from CO and H$_2$O on Fe$_2$O$_3$, CH$_3$OH synthesis on ZnO-Cr$_2$O_3, and CO$^{18}$O and CO formation from CO$^{18}$ and CO$_2$ (O-exchange) on Fe$_2$O$_3$. Meanwhile, authors of [22,23] supposed that the applicability of the power-law kinetic equations for description of kinetic data suggests a surface heterogeneity and that these equations cannot be deduced from notions on homogeneous surfaces. Thus, no notions on surface heterogeneity are necessary for description of kinetics of these stationary catalytic processes.

Thus, no formal analytical descriptions are available to support the conclusion about any manifestation of surface heterogeneity in stationary catalysis and adsorption. Apparently, the most reliable, if not
unique, way to clarify this question lies in measurements of the molar heats of adsorption at different surface coverages by adsorbates. If biographic or induced heterogeneities are significant, they should manifest themselves in the same way, namely, the heats of adsorption of gases should decrease as the surface coverages by these gases increase.

Meanwhile, constant or almost constant molar heats of adsorption in wide ranges of coverages were obtained by about 20 scientific groups under usual vacuum and under ultra-vacuum conditions for about 40 adsorbent-adsorbate systems, including powder and film adsorbents. These studies are listed in [9,19]. They contradict the notions of the significant effect and film adsorbents. These studies are listed in [9,19]. We do not consider systematically possible defects of ultra-vacuum measurements. We will demonstrate only one example showing that spectacular procedures alone do not provide a high reliability of measured results. In [27], coverage-dependent molar calorimetric heats for CO adsorption on thin Ni/211/films at about 300 K were obtained; 50 ms pulses of CO were input to the film with 2.5 s intervals, and the adsorbed gas amount was calculated through the difference between the integral gas amounts in the incident and reflected CO beams. However, if the beam diameter is much lesser than the film size, the surface-mean coverage differs from the under-beam surface coverage and, if the beam diameter is near the film size, a portion of the gas molecules falls beside the crystal. As for the reflected beam, it is partially dissipated by the crystal steps and other defects and some of the reflected molecules can not be fixed by the sensor of the reflected beam. In addition, it is impossible to say a priori that the 2.5 s interval between the gas inputs is sufficient for equilibration of the ads gas through its surface migration. None of these technical features is discussed in [27].

However, the most principal doubts in these results are caused by the following. It is well known that crystalline Ni is capable of transforming to NiC$_3$ and to Ni(CO)$_4$ (the boiling temperature of Ni(CO)$_4$ is equal to 315 K). Usual methods for NiC$_3$ and Ni(CO)$_4$ production are CO interaction with Ni at about 500 and 320–360 K, respectively [28]. The possibilities of forming NiC$_3$ (surf) and Ni(CO)$_4$ (gas) or Ni(CO)$_4$ (surf) at 300 K should not be ignored a priori at rather high surface coverages by CO. The reactions for NiC$_3$ and Ni(CO)$_4$ production can introduce side heat effects that are comparable with those corresponding to CO adsorption. Besides, a “fresh” Ni surface...
can arise as a result of Ni(CO)$_4$ desorption and the amount of CO adsorbed can differ significantly from that determined from the difference between the incident and reflected CO-beams. These side processes are not discussed in [27]. Meanwhile, it is not impossible that their contributions to the heat effects are significant and coverage-dependent.

It should be noted that the molar heats of CO adsorption at Ni/111/[29] and Ni/100/[30] calculated from isosters measured under ultra-vacuum conditions are coverage-independent over rather wide ranges of surface coverage, and the initial molar heats differ significantly from those presented in [27].

Apparently, the above-mentioned energy exchange acts under the condition that the metal crystals are so large-sized that the number of surface atoms is well over the number of the bulk ones. Otherwise, chemisorption associated with a partial polarization of the adsorbed particles may change noticeably the number of electrons in the body of the crystal and thus change its characteristics, including the catalytic and chemisorption ones. For very fine crystals, a dependence of the heat of chemisorption on the coverage may be expected [31,32] (see [19]). However, it is unlikely that such fine crystals could exist in reality in the course of catalytic and adsorption processes proceeding stationarily at elevated temperatures.

Doubts about the validity of the notions on any significant effect of surface heterogeneity on the catalytic and adsorption properties of solids and about the usefulness of application of these notions to describing and simulating actual catalytic and adsorption processes are repeatedly expressed from different viewpoints (e.g., [9] and [33–40]).

We showed that the most reliable, if not unique, way to confirm or disprove these doubts lies in measurement of the heats and rates of adsorption and desorption. Therewith, the measurements performed with samples being in the states corresponding to those occurring in actual reacting media are most informative. The ways allowing achievement of such states under conditions of adsorption measurements are nontrivial. Indeed, identification of these states is a complicated problem, and measurements in such states are rather difficult because the surfaces contain different adsorbed particles, which are in accordance with the reaction media of complex compositions. In this connection, we annotate briefly two procedures meant for achieving such states (by the examples of catalysts for the NH$_3$ and CH$_3$OH syntheses) and two sets of calorimetric results relating directly to the problems considered in this section.

The technical and procedural approaches described in Section 2 were applied in these studies. The Fe/K$_2$O/Al$_2$O$_3$ and CuO/ZnO/Al$_2$O$_3$ catalysts were slowly reduced under static conditions by small portions of H$_2$ (and also CO in the case of the CuO/ZnO/Al$_2$O$_3$ catalyst) dosed one-by-one under delicate conditions preventing the possibility of sintering (the procedures applied to the former and latter catalysts are detailed in [41,42] and in [9], respectively). From time to time, we dosed small portions of NH$_3$ and CH$_3$OH vapors to the former and latter catalysts, respectively. At the beginning of the reduction, the doses of NH$_3$ and CH$_3$OH vapors contacting with the former and latter catalysts, respectively, reacted with the catalysts entirely. At some degrees of the reduction, the NH$_3$ and CH$_3$OH doses began to react not entirely, then, H$_2$ and H$_2$ with CO$_2$ were observed over the NH$_3$ and CH$_3$OH catalysts, respectively. The catalyst states thus obtained were influenced by the gaseous media, which were close to the equilibrium ones, and the catalyst surfaces contained the corresponding adsorbed particles. Therefore, we consider that these states approximated the catalyst states occurring in the course of actual catalytic processes. We list here the calorimetric results, showing that the surfaces of the catalysts thus obtained are homogeneous in their adsorption properties. These results are as follows.

On the reduced Fe/K$_2$O/Al$_2$O$_3$ catalyst:

1. The molar heats of N$_2$ adsorption computed on the basis of the measured heats of NH$_3$ decomposition to adsorbed nitrogen and gaseous H$_2$ at 470 K are constant in a rather wide range of coverages [19,43].
2. The molar heats of H$_2$ desorption at 470 K from the adsorbed layer containing hydrogen and nitrogen are constant and independent of the hydrogen and nitrogen amounts in the adsorbed layer [19,43,42].
3. On the reduced CuO/ZnO/Al$_2$O$_3$ catalyst [44]:
   1. The molar heats of O$_2$ adsorption are independent of the surface coverage in a wide range of its variation, and the rate of adsorption is described with an equation deduced for the cases of adsorption of each molecule at two centers of a homogeneous surface.
   2. The molar heats of H$_2$ adsorption are independent of the adsorbed amount.
   3. The molar heats of CO$_2$ chemisorption are independent of the adsorbed amount.
The results obtained with the reduced CuO/ZnO/Al₂O₃ catalyst are detailed in [3,9].

Measurements of the heats of N₂ adsorption on the Fe/K₂O/Al₂O₃ catalysts represent a rather complicated problem, and the method applied by us has principal procedural peculiarities.

At about 500–550 K, N₂ chemisorption proceeds very slowly and the heat of adsorption can not be measured quite exactly. At higher temperatures and low pressures of N₂, the equilibrium coverage is too small and the adsorbed amounts can not be measured rather exactly. And, in conclusion, at high pressures and high temperatures, the adsorbed amounts and the heats of adsorption can not be measured quite exactly by the volumetric method because the pressure reduction caused by the adsorption is too small. An increase in the mass and thickness of the catalyst layer can not help in solving this problem because of the diffusion limitation of adsorption in thick catalyst layers, the slowness of approaching to the adsorption nitrogen distribution along the catalyst layer. Therefore, the molar heats of N₂ adsorption are computed on the basis of measurements of the heats of NH₃ decomposition to adsorbed nitrogen and gaseous H₂ at about 470 K. Under such conditions, H₂ can be adsorbed as such and as hydrogen-nitrogen radicals and, in addition, can be absorbed within the iron surface layers [41,43]. Under the condition of a rather high N/H ratio, hydrogen is bonded almost entirely with surface nitrogen [43]. Joining together an empty volume and the volume over the catalyst containing the N-H adsorbed radicals leads to H₂ desorption from the radicals. The molar heat of H₂ desorption from these radicals Q(H₂)=51.5 kJ/mol and does not depend on the H and N amounts on the surface. The molar heats of N₂ adsorption (Q(N₂)) were computed with the formula Q(N₂)=23.5+(q−nQ(H₂))/m on the basis of measurements of the heat (q) liberated as a result of the interaction of small NH₃ amounts with the catalyst. In this formula, m and n are the adsorbed moles of N₂ and H₂, respectively. In order to minimize the effect of the inaccuracy in Q(H₂) determination on the measured Q(N₂) values, the measurements were performed under conditions when H₂ was desorbed from the surface layer almost entirely.

The consideration presented in this section of the paper allows us to believe that the available notions of a principal effect of surface heterogeneity on chemisorption are not justified and had originated from imperfections of the experimental techniques applied earlier.

3.2. Deep adsorption: is it an artifact or a reality?

In this section, one more experimental problem requiring modernization of the common techniques and procedures is considered.

A lot of authors consider their data on gas adsorption on metals in terms of “subsurface” adsorption (for example, [45–47]). Such a consideration has its backgrounds in [48–50] and in still earlier studies [51,52]. The studies [48–52] contain statements that, under a pressure of no more than 0.25 hPa, the O₂ amounts that can be adsorbed on Pt foils [48] (the apparatus is described in [53]), powdery Ag [50], Au foils [49], and powdery Cu [51] or the H₂ amount that can be adsorbed on powdery Fe [52] multiply exceed the gas amount corresponding to the full coverage of one monolayer. In [49,50], the results of [48–52] were termed the “deep” adsorption. The phenomenon of subsurface adsorption for O₂ on Cu and H₂ on Fe was supported (the last, only qualitatively) in [54]. However, no subsurface oxygen adsorption was observed on Au in [12] and on Ag in [3,11,14]. As far as we know, no work has supported the concept of 300-monolayer oxygen adsorption by Pt. Notice that “deep” adsorption and “subsurface” adsorption differ from each other in their behaviors. Moreover, physically distinct phenomena were identified in [50] as “deep” adsorption. In [45–47], the notion of subsurface adsorption is used as a possible explanation for experimental data obtained by the low-energy electron diffraction (LEED), temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS) techniques applied to the O₂-Ag system. The data presented give grounds to believe that the O₂ amounts adsorbed in these studies do not exceed the capacity of 1–2 monolayers. Generally speaking, they could be explained as a combination of the processes of surface adsorption and subsurface dissolution in the context of the well-known notions on gas-metal processes [55]. The notions of “deep” adsorption are not necessary for understanding the results of these studies. Moreover, we will show below that these data could be explained with-
out the notion of subsurface adsorption. In [48–50], the “deep” adsorptions of $O_2$ on Pt (1073 K, 0.13 hPa), Au (673 K, 0.25 hPa), and Ag (523 K, 0.25 hPa) are as extensive as 300, 12, and 5 monolayers, respectively. There is no possibility to explain these data by either surface adsorption or gas solubility within the bulk materials. The gas solubilities in these systems are smaller by a factor of $10^3$–$10^4$ (see [55]). However, phase oxidation is also impossible because the change in free energy for oxidation is positive. In [51], $O_2$ adsorption also exceeds significantly the monolayer capacity; however, the case in this point is adsorption on a metal that is characterized by a negative change in the standard free energy during phase oxidation. The case in [52] is the $H_2$ adsorption on Fe, which is incapable of forming phase hydrides under the experimental conditions. However, the H-atoms are very small as compared to the tetrahedral cavities of the Fe lattice and to the O atoms, and hydrogen solubility in Fe is significantly higher than the oxygen solubility in Ag or Au. In addition, according to [39,43,54], the total amount of hydrogen in Fe does not exceed the monolayer capacity, and can be explained by a combination of gas adsorption on the surface and gas dissolution within the solid. According to our interpretation of the experimental data obtained at about 450 K, the process of gas dissolution by Fe extends to only 1–2 nearest subsurface monolayers, in which some surface properties can still reveal themselves.

For the following discussion of the nature of “deep” adsorption to be more fruitful, we will note briefly some technical and procedural peculiarities of [48–50], and will annotate some results obtained in the same systems by other authors.

In [48–50], greased taps were used and the ampoules with the samples were joined to the apparatuses through the packages shown in Figures 3(b) and 3(c). In these papers, no mentions have been made of the controlling of the amounts condensed in the trap 5 and of the considering of the $CO_2$ and $H_2O$ formation from the grease vapor and oxygen during the experiments on $O_2$ adsorption. Besides, the pretreatment of the samples was performed with no control of the products of reduction and degassing. Therefore, it is impossible to estimate the quality of the pretreatment of the metal samples.

It is mentioned above that, according to [11,56] and [10], the amounts of $O_2$ capable of being chemisorbed on powdery Ag (measured in [11] at 380–470 K and a pressure up to 0.34 hPa) and Au (measured at about 400 K and 0.08 hPa), respectively, are limited by a gas volume corresponding to the capacity of one monolayer. The heats of $O_2$ chemisorption on Ag and Au are given in Figures 4 and 5, respectively. Figure 4 indicates the occurrence (at 465–469 K) of two levels of the heats of $O_2$ adsorption, about 200 and 70 kJ/mol with a step at a surface coverage of about 70 mm$^3$ ntp/m$^2$. Figure 4 presents the adsorption heats measured in [11] and computed in [56] from isotherms. It is seen that the results of the two papers are similar to each other. We propose the following adsorption mechanism [11]:

$$8Ag + O_2 \leftrightarrow 2Ag_4[O]_{ads} \quad (7)$$
$$2Ag_4[O]_{ads} + 3O_2 \leftrightarrow 8Ag[O]_{ads} \quad (8)$$

The sign $\leftrightarrow$ means that the steps are partially reversible. Under the experimental conditions, the system goes to the equilibrium slowly.

For step (7), the heat of chemisorption is 200±10 kJ/mol. This step goes up to a coverage of about 70 mm$^3$ ntp/m$^2$, i.e., up to a quarter of the total monolayer capacity. Step (8) is characterized by a heat effect of about 210 kJ/mol, i.e., the molar heat of chemisorption is 70 kJ/mol. For the integral process, i.e.

$$2Ag + O_2 \leftrightarrow 2Ag[O]_{ads} \quad (9)$$

the heat effect is 102.5 kJ/mol. The heat effect per mole of $O_2$ is much higher for (7) than for (8). There-
Therefore, under rather high temperatures, when the surface processes are proceeding so fast that the equilibrium can be achieved, step (8) begins after the termination of step (7). If the temperature is low or the O\textsubscript{2} amount in each experiment is large, the molar heat effects accompanying adsorption can range from 70 to 200 kJ/mol, depending on the preadsorbed amount, the volume of the O\textsubscript{2} dose, and the time interval between subsequent doses. In addition to the results of [56], the following data on the heats of adsorption (kJ/mol) are available: about 167 (/110 face, isothermal thermodesorption [42]), 146–188 (/111 face, thermodesorption [45, 57]), and 175 (powder, computation from isotherms [58]). The study of oxygen isotopic exchange on powdery Ag at 473 K allowed the author of [59] to conclude that Ag surfaces revealed themselves as homogeneous and the heat of O\textsubscript{2} adsorption was 110 kJ/mol (near the heat effect of (9)). All these values are between 70 and 200 kJ/mol.

The O\textsubscript{2} adsorption is reversible, namely, it increases with increasing pressure and decreasing temperature. For example, at 465 K, it was observed that the pressure and surface coverage were 0.217 hPa and 196 mm\textsuperscript{3} ntp/m\textsuperscript{2}, respectively, (for comparison, at the same temperature, a surface coverage of 73 mm\textsuperscript{3} ntp/m\textsuperscript{2} was observed at 0.014 hPa). Thus, the O\textsubscript{2} pressure over Ag increases rather quickly with the oxygen coverage. The same effect was observed in [60].

At 415, 464, and 469 K, under near-equilibrium conditions, adsorption of 258, 196, and 160 mm\textsuperscript{3} ntp/m\textsuperscript{2} corresponds to O\textsubscript{2} pressures of 0.096, 0.211, and 0.276 hPa, respectively [11]. Thus, at 469 K and 0.276 hPa, i.e., near the O\textsubscript{2} pressures at which the “deep” adsorption is observed in [50], the adsorbed amount of O\textsubscript{2} does not exceed the monolayer capacity. It was stated that, as the temperature increases, the chemisorbed amount decreases. These results mean that no “deep” adsorption occurs at 469 K and at higher temperatures.

Taking into account the differences in the techniques, procedures, and samples, we believe that the results of all studies considered above confirm each other. These studies do not support, among other things, the notions of deep O\textsubscript{2} adsorption on Ag under low pressures.

The data on “deep” adsorption of O\textsubscript{2} on Au [49] are all the more questionable as compared to those on Ag. Meanwhile, nobody has revealed up to now the real cause of so large adsorbed amounts of O\textsubscript{2}. In fact, a semi-centennial discussion is being continued on the question whether or not Au is capable to chemisorb one monolayer of oxygen at elevated temperatures and low pressures. We believe that if we proved in [12] that O\textsubscript{2} adsorption proceeds and goes with a coverage-independent molar heat of about 430 kJ/mol (see Figure 5). The results are well reproduced with two powdery samples at 393 and 413 K. The heat of chemisorption does not depend on the degree of surface coverage by oxygen up to 200 mm\textsuperscript{3} ntp/m\textsuperscript{2} and is equal to 429.9 kJ/mol at 393 K and 419.4 kJ/mol at 413 K. The standard deviations are equal to 18.0 kJ/mol (4.1%) and 18.8 kJ/mol (4.5%) for the data measured at 393 and 413 K, respectively. The scatter in the molar heats of chemisorption for

![Figure 5. Heats of oxygen adsorption on powdery gold. (a) not corrected molar heats of oxygen adsorption, sample 1 (413 K) [63]; (b) corrected molar heats of oxygen adsorption [12]; circles are obtained with sample 1, squares are obtained with sample 2 (393 K), crosses give molar heats of oxygen adsorption computed from the heat effects measured for the reaction H\textsubscript{2}+0.5 O\textsubscript{2,ads}=H\textsubscript{2}O and the tabulated standard enthalpy for the reaction H\textsubscript{2}+0.5O\textsubscript{2}=H\textsubscript{2}O, lower and upper dashed lines give the mean values for samples 1 and 2, respectively, and solid line gives the overall mean value](image-url)
each of these two measurement series is determined by the errors in the measured heat effects and amounts of adsorbed oxygen. A difference of 5.0% between the mean values of the molar heats measured at 393 and 413 K is within possible systematic errors. These results of [12] are neither confirmed nor refuted up to now. Apparently, the Au samples were rather pure. The certified total contents of heavy metals in the source reagents used for \(\text{Au(OH)}_3\) precipitation is less than 0.01%. The impurity Ag atoms can occupy no more than 0.05% of the surface. It was analyzed on the Au surface after studies of \(\text{O}_2\) adsorption. A special procedure consisting of dissolving the surface layer of Au in nitric acid and subsequent spectral analyses of the solution was applied. The pretreatment of the Au samples before adsorption is specified above in Table 2. The adsorption did not exceed rather slowly. Thus, in order to measure the adsorbed amounts. We believe that difficulties occurring on the ways for solving these problems are the causes hampering the discovery of \(\text{O}_2\) adsorption on Au in [61] (under ultra-vacuum conditions at elevated temperatures) and also in [62]. In [63], it was shown that the sensitivity of the usual ultra-vacuum technique is apparently insufficient for measuring the rate of \(\text{O}_2\) adsorption on Au. The failure of detecting \(\text{O}_2\) adsorption in [62] was possibly caused by a too small surface area or by the insufficient reduction of the sample.

In our opinion, the mechanism of \(\text{O}_2\) chemisorption is as follows:

\[
4\text{Au} + \text{O}_2 = 2\text{Au}_2[\text{O}]_{\text{ads}} \tag{10}
\]

\[
2\text{Au}_2[\text{O}]_{\text{ads}} + \text{O}_2 = 4\text{Au}[\text{O}]_{\text{ads}} \tag{11}
\]

The oxidized Au surface is capable of chemisorbing \(\text{H}_2\). After chemisorption of \(\text{O}_2\) and \(\text{H}_2\), the Au surface chemisorbs additional \(\text{O}_2\) faster and with a somewhat higher heat effect than before the \(\text{H}_2\) adsorption. The results are well reproduced with two samples at 393 and 413 K (Figure 5). However, there are neither experimental confirmations nor physical prerequisites for multilayer “deep” adsorption of \(\text{O}_2\) on Au.

The “deep” adsorption of 300 monolayers of \(\text{O}_2\) on Pt under conditions described in [48] is also not confirmed by subsequent experiments.

It would appear reasonable that a universal technical cause leading to the overestimation of adsorbed amounts and to the notions of “deep” adsorption exists. In the following section, we will consider the most probable cause initiating these notions.

### 3.3. Adsorption-chemical equilibriums: effect of technical imperfections on data on heats of adsorption

Gas-surface systems go to the equilibrium states through both adsorption-desorption and surface migration processes. Equilibriums resulting from reactions between gaseous substances and other substances adsorbed on surfaces are termed as “adsorption-chemical equilibriums”. Measurements of the constants of such equilibriums were used for computing the heats of adsorption of some gases (e.g., [23, 61, 64]). As an example, consider the equilibriums:

\[
\text{O}_{\text{ads}} + \text{H}_2(\text{gas}) \equiv \text{H}_2\text{O}(\text{gas}) \tag{12}
\]

\[
0.5\text{O}_2(\text{gas}) + \text{H}_2(\text{gas}) \equiv \text{H}_2\text{O}(\text{gas}) \tag{13}
\]

For any fixed coverage (\(\theta\)), the volatility of oxygen is determined by the ratio \(p(\text{H}_2\text{O})/p(\text{H}_2)\) (\(p\) is the pressure and the sign \(\equiv\) means equilibrium). According to equation (13), we can write

\[
\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)p(\text{O}_2)^{0.5}} = K \tag{14}
\]

Thus,

\[
p(\text{O}_2)^{0.5} = \frac{p(\text{H}_2\text{O})}{Kp(\text{H}_2)} \tag{15}
\]

For any chosen temperature and \(\theta\), authors of [23, 61, 64] substitute the tabulated \(K\) value and experimental value of \((p(\text{H}_2\text{O})/p(\text{H}_2))\) and thus obtain \(p(\text{O}_2)\). By varying \(\theta\), they obtain a number of \(p(\text{O}_2)\) values, i.e., the isotherm of \(\text{O}_2\) adsorption on the surface under study. Isotherms thus obtained were used for computing the heats of \(\text{O}_2\) adsorption. These authors consider that the reduced oxide surfaces correspond to the zero adsorption and that the catalyst surface is reduced fully by an amount of \(\text{H}_2\) corresponding to the stoichiometry of reaction (12); therewith, the monolayer amount of oxygen is pre-evaluated from measurements of the specific surface area of the sample under study. Results of some of these studies are given in Table 3 after their scaling to the molar heats of \(\text{O}_2\) adsorption, kJ/mol \(\text{O}_2\) (in
some original studies, these values are presented in terms of the energy of binding of the adsorbed atoms with the surface). They are used in different discussions (for example, [59]). Meanwhile, some results computed from the adsorption-chemical equilibriums are questionable and are in need of checking.

It is evident that the heat of \( \text{O}_2 \) adsorption on any oxide can not be higher than the heat of \( \text{O}_2 \) adsorption on the metal reduced from this oxide and should be less than the standard heat of oxidation of this metal. Meanwhile, the standard heats of oxidation of Co (411 kJ/mol \( \text{O}_2 \)) and Cu (311 kJ/mol \( \text{O}_2 \)) to \( \text{Co}_3\text{O}_4 \) and \( \text{CuO} \) and the heats of \( \text{O}_2 \) adsorption on Co and Cu (see Table 3) are significantly smaller than the values obtained in [65] for the heats of \( \text{O}_2 \) adsorption on \( \text{Co}_3\text{O}_4 \) (517 kJ/mol \( \text{O}_2 \)) and \( \text{CuO} \) (507 kJ/mol \( \text{O}_2 \)). The values proposed in [65] as the heats of \( \text{O}_2 \) adsorption on \( \text{Co}_3\text{O}_4 \) and \( \text{CuO} \) are also higher than those obtained in [3,67–69] and in [3,54,70,71] on corresponding metals used in the form of evaporated films under ultra-vacuum conditions [67–69] or powders under high-vacuum conditions [3,54,69,71] (see Table 3). The value proposed in [65] as the heat of \( \text{O}_2 \) adsorption on Fe\( _3\text{O}_4 \) (522 kJ/mol \( \text{O}_2 \)) is close to the heat of \( \text{O}_2 \) adsorption on Fe films (573 kJ/mol \( \text{O}_2 \)) and to the standard heat of oxidation of iron (558 kJ/mol \( \text{O}_2 \)). The heat of \( \text{O}_2 \) adsorption on metal Ag obtained in [62,65] by the method of adsorption-chemical equilibrium is significantly higher than that obtained from the calorimetric [3,71], thermo-desorption [45], and isosteric [56,58] techniques. The heats of \( \text{O}_2 \) adsorption measured on Pt in [65] and in [62] with the same method of adsorption-chemical equilibrium give the results (561 and 225 kJ/mol), which differ from each other too significantly.

<table>
<thead>
<tr>
<th>( X )</th>
<th>( \theta )</th>
<th>( Q/(\text{kJ/mol}) )</th>
<th>( T/K )</th>
<th>( Q/(\text{kJ/mol}) )</th>
<th>( T/K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_3\text{O}_4 )</td>
<td>0.1–0.9</td>
<td>522±40 [65]</td>
<td>673</td>
<td>573 [67]</td>
<td>273</td>
</tr>
<tr>
<td>( \text{Co}_3\text{O}_4 )</td>
<td>0.1–0.9</td>
<td>517±26 [65]</td>
<td>673</td>
<td>427 [67,68]</td>
<td>273</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td></td>
<td>460 [69,3]</td>
<td>298</td>
</tr>
<tr>
<td>( \text{CuO} )</td>
<td>0.1–0.9</td>
<td>507±10 [65]</td>
<td>473</td>
<td>335 [70]</td>
<td>298</td>
</tr>
<tr>
<td>( \text{V}_2\text{O}_5 )</td>
<td>0.1–0.6</td>
<td>561±18 [65]</td>
<td>873</td>
<td>365 [54,3,71]</td>
<td>373,383</td>
</tr>
<tr>
<td>Pt</td>
<td>0.1–1.0</td>
<td>561±16 [65]</td>
<td>873</td>
<td>225 [62]</td>
<td>573</td>
</tr>
<tr>
<td>Ag</td>
<td>0.0–1.0</td>
<td>481±20 [65]</td>
<td>473</td>
<td>two-level step: 200 and 70 [3]</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>167 [72]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>455 [62]</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>188–146 [45]</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td>211 [66]</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ni</td>
<td>469±22 [23]</td>
<td>673</td>
<td>481 [67]</td>
<td>273</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>486 [68]</td>
<td></td>
</tr>
</tbody>
</table>

The values are computed from adsorption-chemical equilibriums for metals and oxides (A-Ch), or measured calorimetrically and computed from isotherms for the corresponding metals (Cal).

The procedures used for the pretreatment of the samples do not allow rather exact identification of the samples just before the experiments on adsorption-chemical equilibrium. For example, the samples of \( \text{V}_2\text{O}_5 \), \( \text{Fe}_3\text{O}_4 \), and \( \text{Co}_3\text{O}_4 \) were degassed before the experiments at 623 K and a pressure of 1 mPa and were not oxidized subsequently; so the degrees of reduction of their surface layers are unknown. The samples of Ag and Cu oxides were dried at a temperature as low as 473 K. At this temperature, H\(_2\)O and CO\(_2\) could not be removed fully from Ag prepared from Ag\(_2\text{CO}_3\) (see Table 1) and H\(_2\)O could not be removed fully from CuO (see Section 2.2.).

It is difficult now to identify reliably the experimental peculiarities making questionable the data obtained with the method of adsorption-chemical equilibrium. The possible principal causes of such a situation are as follows: the use of the glass apparatuses similar to those shown in Figures 3(b) and 3(c); neglect of afteroxidation for the oxide samples after their
preliminary treatment and of the effect of grease oxidation by surface oxygen; insufficient cleaning of oxygen from the metal samples before the experiments; absence of any control over the degree of removal of biographic $\text{H}_2\text{O}$ and $\text{CO}_2$ from the samples and over $\text{CO}_2$ desorption during the experiments; and insufficient consideration of $\text{H}_2$ chemisorption on the surfaces covered partially with oxygen.

3.4. Seeming artifacts

Figure 6(a) presents data on heats of $\text{H}_2$ chemisorption measured at 463 K on a NiO sample [54]. These data are measured at any one sample in four series (A, B, C, and D) of successive experiments. Before each of the experimental series, the catalyst contained different amounts of hydrogen and oxygen. Before the first experimental series (A), this sample was dried incompletely. Nevertheless, the state at the beginning of the series A is taken as the standard one. In this state, the hydrogen and oxygen contents in the sample are, by convention, equal to zero. The experimental series on $\text{H}_2$ adsorption alternated with the experimental series on $\text{O}_2$ adsorption. Beginning from the first experiment of the series A, we controlled the content of hydrogen and oxygen in the sample by considering the amounts of adsorbed $\text{H}_2$ and $\text{O}_2$ and desorbed $\text{H}_2\text{O}$ in the course of each experiment. As a consequence of $\text{H}_2\text{O}$ desorption, the catalyst state during some experiments have negative hydrogen and oxygen amounts relative to the standard state. Table 4 contains information on the hydrogen and oxygen amounts before and after each experimental series. The vertical lines in the figure indicate the maximum chemisorption capacity measured in each of the series A, B, C, and D. The chemisorption capacity is different for different series and the heat of chemisorption is not determined uniquely by the chemisorbed amount of $\text{H}_2$.

![Figure 6](image)

**Figure 6.** Heats of hydrogen chemisorption on a sample of nickel oxide measured at 463 K in the series A (light circles), B (black circles), C (black squares), and D (light squares); before the first series (A), the sample was dried incompletely. (a) The heats of chemisorption vs. the hydrogen amount in the sample; the vertical lines indicate the maximum chemisorption capacity for each series; between the A and B, B and C, and C and D series, oxygen adsorption was performed. (b) The heats of chemisorption vs. the sum of hydrogen and oxygen amounts in the sample.

| Table 4. Oxygen and hydrogen amounts in the NiO sample at the beginning and end of each of four series of $\text{H}_2$ adsorption |
|-----------------|-----------------|-----------------|
| **Series** | **At the beginning of the series (mm$^2$ ntp/m$^2$)** | **At the end of the series (mm$^2$ ntp/m$^2$)** |
| | $\text{O}_2$ | $\text{H}_2$ | $\text{O}_2$ | $\text{H}_2$ |
| A | 0.0 | 0.0 | -8.3 | -33.0 |
| B | -1.6 | -23.5 | -3.9 | +26.5 |
| C | +7.8 | 0.0 | +1.2 | +20.5 |
| D | +9.0 | +10.0 | +5.3 | +20.0 |

The sample before the first series A was dried incompletely. Signs (−) or (+) mean that the amount is less or more, respectively, than that in the standard state of the sample before the series A.“ Between the series A and B, B and C, and C and D, experiments on $\text{O}_2$ adsorption were performed with no contact of the sample with the atmosphere and with control of gradual changes in the oxygen and hydrogen amounts in the sample.
Figures 7(a) and 7(b) show the maximum CO amounts chemisorbed on two samples (samples 1 and 2, respectively) of the CuO/ZnO/Al₂O₃ catalyst applied in different oxidized forms, which differ not critically from the standard oxidized state. The maximum chemisorption is determined at 273 K through measurements of the rates of CO chemisorption from the subsequent doses of the adsorbate. For each of the samples, two series of measurements were performed. Each of the samples was somewhat reduced between two series on CO chemisorption. The initial CO pressure in each of the doses was about 0.13 hPa (the results of Figure 7(a) are published in [73]). It is seen that the chemisorption capacity of each of the samples varies many-fold from series to series; i.e., the maximum chemisorbed amount is not a single-valued function of the surface coverage.

The data of Figures 6(a), 7(a), and 7(b) show up seemingly to be artifacts. However, this is not the case, and the peculiarities of these data contain rather surprising information on the mechanism of adsorption (see the following Section where Figures 6(b) and 7(c) will be interpreted).

3.5. Principal technical problems of adsorption measurements at silica-aluminia, zeolite, and similar catalysts

In the last two decades, silica-aluminia and zeolite catalysts and adsorbents are the most abundant of the objects for adsorption calorimetric measurements (for example, [74–87]). These measurements have a sharply defined orientation: to classify the solids relative to the heats of adsorption of definite chemical sensors and to associate this classification with the levels of chemisorption and catalytic activities of these solids in acid-base reactions. As sensors, several standard adsorbates such as ammonia, pyridine, and some other are applied. This theme merits special and detailed consideration, which is impossible in the framework of this paper. Below, we shall take only a quick look at some principal peculiarities of the calorimetric results relating to such adsorbents.

A principal peculiarity of the systems containing silica-aluminia and zeolite as adsorbents is that the calorimetric data obtained for such systems demonstrate, with rare exceptions, a significant decrease in the heat effect with increasing adsorbed amount. One of the exceptions is in [76], presenting a constant heat of pyridine adsorption on NaH-modernite against the adsorbed amount. This result can mean that, under the experimental conditions, pyridine adsorbs predominantly on sites of one kind and the heat of its adsorption on the other sites is so small that the contribution of adsorption by them is small, or pyridine adsorbs on all adsorption sites of this solid with approximately the same molar heat. However, the adsorption heat - adsorbed amount dependences have usually several steps which are pronounced more or less clearly. The steps are explained by the occurrence of surface sites of different chemical nature and acidic strength. For similar adsorbent-adsorbate systems, the reproducibility of these dependences measured in different studies leaves something to be desired. The adsorption heat - adsorbed amount dependences have usually several steps which are pronounced more or less clearly. The steps are explained by the occurrence of surface sites of different chemical nature and acidic strength. For similar adsorbent-adsorbate systems, the reproducibility of these dependences measured in different studies leaves something to be desired. The adsorption heat - adsorbed amount dependences with maxima and minima are also available. It is generally taken that the higher the heat of adsorption of gaseous bases (such as NH₃) and the larger the num-
ber of the catalyst sites with a high heat of adsorption, the higher the activity of this catalyst in the so-called acid-base reactions. However, it is shown [88] on the basis of computation of the turnover frequency that the catalytic-activity comparisons based entirely on acid strength may not be valid when the catalysts in question are of different kinds [89].

The reproducibility of calorimetric measurements in the systems under consideration is influenced to a greater or lesser extent by all technical and procedural features considered in Section 2. However, in our opinion, prevention of the controlling of adsorption processes (or desorption processes, when they are studied) by diffusion takes on primary significance. This peculiarity is associated with two, i.e., structural and physico-chemical, properties of such systems. First, the solids in question are characterized by very large specific surface areas and fine pores or honeycomb structures with extremely narrow clearing holes. Second, these solids are isolators or almost isolators and, therefore, the energy exchange between individual atoms at usual temperatures of adsorption measurements proceeds rather slowly; and besides, these solids are formed by atoms of different chemical nature having different nearest surroundings. It can be expected that atoms of such solids maintain their individual chemical specificity, unlike atoms of well-conducting solids where collective properties of crystals prevail. In Langmuir’s terms [90], surfaces of the solids in question should be considered, apparently, as surfaces consisting of sites of several different kinds and different adsorption abilities. If this is the case and the equilibrium in the course of adsorption is achievable, the sites of different kinds and different adsorption abilities should be covered kind by kind in the order of decreasing adsorption ability, and thus the adsorption heat - adsorbed amount dependence should be staircase-like. This order can be disturbed by two phenomena of a diffusion nature: (1) predominant adsorption of the adsorbates by the frontal surface of the adsorbent layer with a slow diffusion of the adsorbates along the adsorbent layer during a time period beyond the framework of the experiment, and (2) adsorption of the adsorbates on the outer surface of the adsorbent and at the entries of the pores, with subsequent slow lateral diffusion to the sites of maximum adsorption ability. If this consideration is correct, the maxima in the adsorption heat - adsorbed amount dependence are artifacts. However, it should be stipulated that our consideration takes the entropy of adsorption at the sites of different kinds to be the same. Otherwise, the last conclusion can be put under question. In any case, it is desirable to make the adsorbent layer as thin as possible and to continue each experiment after termination of adsorption as long as the calorimeter allows for measurements of the heat effects.

3.6. Heats of water vapor sorption by “Nafion”-like perfluorinated polymers: an effect of apparatus walls

Figure 8 contains results of calorimetric room-temperature measurements of the molar heats of water vapor sorption by the sulfurized perfluorinated polymer materials of the “Nafion” type. In these materials, the main polymer chains consist of perfluoroethylene units, while the side-chains contain -SO₃H groups and have the following composition:

\[-[O - CF₂ - CF(CF₃)]ₘ-O - CF₂ - CF₂ - SO₃H\]

![Figure 8](image-url)
The sorbed water molecules are located around each -SO$_2$H group. The water amount in the sample is characterized by the value of the molar ratio, \( n = \frac{n\text{H}_2\text{O}}{\text{(-SO$_2$H)}} \). The solid straight line corresponds to the heat of water condensation \( Q_L \) at the liquid pure-water surface at 298 K. The data of [91] on the heat effect of the one-by-one addition of water vapor molecules to an H$_2$SO$_4$ molecule in solution are given for comparison. The dotted curve is plotted on the basis of the data measured by us [92,93]. The solid curve is obtained in [94,95] as a result of calorimetric measurements performed at room temperature with a “Richard Ejraud” calorimeter combined with a B60 “Setaram” beam balance. It is seen that the solid curve at \( n > 3.5 \) lies significantly below the \( Q_L \) level. In [95], the molar heat of water vapor sorption at \( n = 6.5-8.5 \) is equal to 16.5 kJ/mol only; i.e., it is below the heat of water vapor condensation (44.13 kJ/mol) by about 27.6 kJ/mol. Water vapor sorption can proceed under the condition that the decrease in the Gibbs free energy during the process is smaller than that during vapor condensation at the surface of liquid water. It is beyond reason to wait that, at \( n = 6.5-8.5 \), the partial molar entropy of water within the polymer can be higher than the molar entropy of liquid water by 94.2 J/(mol K) (27600 (J/mol)/(293 K)). Therefore, it may appear that water sorption increases significantly the partial molar entropy of the polymer. However, it seems likely that this result is an artifact.

Our results [92,93] presented in Figure 8 by the dotted curve and by solid sections numerated in correspondence with the numbers of the measurement series differ significantly from the data obtained in [95]. The data in [92,93] (see also [3]) are measured with a FOSKA calorimeter [3] combined with a glass apparatus. The apparatus and procedures are detailed in [17,93].

Most likely, the peculiarities of the data of [95] have the following cause. The principle of weighing with the B60 “Setaram” beam balance is that the balance is brought to equilibrium when the electromagnetic force counterbalances the comparative beam. This force is proportional to the illumination of the photosresitor by the light source. Both the photosresistor and the light source are arranged in the volume from which adsorption proceeds. Apparently, at the surface of the photosresistor, water is adsorbed specifically and the adsorption increases with the humidity. Adsorbed water reflects partially the incident light and thus decreases the effective illumination of the photosresistor. Therefore, in [95], the adsorbed water amounts are overstated and the molar heats computed through division of the heat effect by the adsorbed water amount are understated.

This example can be considered as a revealing of a negative effect of walls of adsorption apparatuses on experimental results.

It might be assumed that our data [92,93] presented in Figure 8 indicate that the surface of the polymer is heterogeneous because the differential heats of sorption decrease significantly as the sorption increases (dotted curve). However, a correlation of these data with the heats of water sorption by liquid sulfuric acid (dashed curve) shows that the dotted and dashed curves are similar. Most probably, water sorption leads to formation of the -HSO$_3$ complexes over the entire sample. For the H$_2$SO$_4$ -H$_2$O system, a similar phenomenon has long been known and the complexes -HSO$_3$H$_2$O, -HSO$_3$2H$_2$O, -HSO$_3$3H$_2$O, and -HSO$_3$4H$_2$O were identified [96].

4. Effect of modernization of high-vacuum adsorption and calorimetric techniques and procedures; comparison with results obtained with ultra-vacuum instrumentation

Figure 9 presents data on hydrogen adsorption on CuO-Cr$_2$O$_3$ spinel. It illustrates the effectiveness of consideration of side H$_2$O and CO$_2$ desorption during adsorption experiments. The experiments were performed in the mid-1970s. A FOSKA calorimeter [3] and a vacuum apparatus (Figure 3(a)) were used. Each experiment was performed at a constant temperature from 393 to 573 K.

The trap 5 (Figure 3) was cooled in some experiments and was at room temperature in the others. The adsorbed H$_2$ amount and duration of adsorption varied widely from experiment to experiment. Therefore, the fraction of H$_2$ oxidized by the catalyst and desorbed as H$_2$O varied widely from one experiment to another. In addition, some amounts of “biographic” CO$_2$ were desorbed in the course of several experiments. The light and black points in Figure 9 are computed on the assumption that all H$_2$ amounts were adsorbed completely and on the basis of the analyses and procedures described in Section 2, respectively.
Application of the improved techniques and procedures to a number of metal powder-gas systems under high-vacuum conditions showed that the molar heats of chemisorption are very close to those measured under ultra-vacuum conditions for the corresponding metal film-gas systems. The comparisons are given in [3] in Figure 6 (Co-film-O\textsubscript{2}, 273 K and Co-powder-O\textsubscript{2}, 298 K) and Figure 7 (Cu-film-O\textsubscript{2}, 273 K; Cu-powder-O\textsubscript{2}, 373 and 383 K; and Cu-component of the reduced CuO/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst, 293 K). The close agreements between the results obtained for the corresponding metal powder-gas and metal film-gas systems highlighted the reliability of both high-vacuum and ultra-vacuum measurements.

One more illustrative example of using the family of technical and procedural modernizations described above is presented by curve 3 in Figure 4 of this paper. This curve represents the results of a pioneering study in the field of calorimetric measurements of molar heats of chemisorption of gases on powders at elevated temperatures in high-vacuum apparatuses [5,97]. We used the adsorption techniques and procedures conventional in the mid-1960s. The heats of O\textsubscript{2} adsorption on Ag powder published by us in these references correlated rather well with the data obtained earlier in [62,65] by other authors on the basis of indirect methods of adsorption-chemical equilibrium. Later, using the improved techniques and procedures described in Section 2.5., we obtained the results presented in Figure 4 (curve 1) and discussed in Section 3.2. Note that curve 1 is below curve 3 as a consequence of elimination of side effects.

Side processes proceed in time. Therefore, the slower the process under study, the more significant the relative contribution of the side heat effect to the heat effect under measurement. Meanwhile, the adsorption rates usually decrease with the coverage. Thus, the relative contribution of the side processes to the measured heat effect increases with the coverage. This is one of the principal causes leading to the apparent decrease in the molar heats of adsorption with the surface coverage. Desorption of CO\textsubscript{2} and H\textsubscript{2}O in the course of the experiments on O\textsubscript{2} adsorption on Au powder (Figure 5) was negligible up to an O\textsubscript{2} adsorption amount of 100 mm\textsuperscript{3}/m\textsuperscript{2}. Then, as the adsorption rate fell, we discovered CO\textsubscript{2} and H\textsubscript{2}O in the trap 5 during each experiment on O\textsubscript{2} adsorption. Ignoring this effect, we obtained the curve given in Figure 5(a), and taking this effect into account, we obtained the corrected curve given in Figure 5(b). As the saying goes, comment is superfluous.

It is generally agreed that the adsorption and calorimetric measurements focused on clarification of the actual mechanism of a catalytic process should be performed under the conditions when the catalyst state is very nearly the same as it is under the conditions of the steady-state catalysis. Meanwhile, precise adsorption measurements of such a kind are rather complicated because of the complexity of experimental identification of these states in themselves and the high requirements to the measurement accuracy for adsorption and side desorption and to the correct interpretation of the heat fluxes measured. The technical and procedural approaches described in this paper and in [1] are capable of promoting clarification of catalytic mechanisms. The corresponding examples relating to the mechanisms of the catalytic CH\textsubscript{3}OH and NH\textsubscript{3} syntheses are detailed in [9] and [35,38], respectively.

In particular, the calorimetric data on chemisorption on the Fe/K\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} catalyst reduced up to a state close to that occurring in the course of NH\textsubscript{3} synthesis allowed thermodynamic estimation of the relative surface concentrations of nitrogen and nitrogen-hydrogen radicals under conditions of industrial synthesis of NH\textsubscript{3}. It was stated that nitrogen prevails at the catalyst surface at about 30 MPa and 770 K, and its surface coverage decreases to 0.5 as the temperature falls to about 600 K [42].

Two examples illustrating the effect of the above-
described technical and procedural modernizations on the clarification of the mechanisms of interaction of gases with surfaces of oxides are given below.

Let us consider Figure 7(c). In this figure, the results of four series of experiments performed with two samples of the oxidized CuO/ZnO/Al$_2$O$_3$ catalyst and presented in Figures 7(a) and 7(b) are given all together. It should be reminded that the states of the samples before the experimental series differ from each other by the surface oxygen content reckoned from the standard oxidized state of each sample. In Figure 7(c), the rates of dose-by-dose adsorption of CO are plotted against the difference between the adsorbed amounts of carbon monoxide ([CO]) and oxygen ([O$_2$]). All experimental points are located around one curve. Adsorption of CO in each of the series terminates when this difference is equal to the same value. This figure allows a clarification of the chemical state of the adsorbed carbon monoxide. If [O$_2$]=0, i.e., as we have taken above, the catalyst surface was oxidized completely up to the standard state, the maximum adsorption of CO was equal to 660 mm$^3$/m$^2$. If the catalyst would be somewhat reduced and [O$_2$] would be below zero, the catalyst should be capable of adsorbing a smaller amount of CO because the maximum value of ([CO]-[O$_2$]) is equal to 660 mm$^3$/m$^2$. Removal of one O$_2$ molecule from the surface decreases its adsorption capacity by one CO molecule. This result means that adsorption of CO leads to the formation of surface carbonate CO$_3^{2-}$.

Another example is H$_2$ adsorption on nickel oxide. Figure 6(b) shows that four experimental series differing by the values of the surface oxygen content at the beginning of these series are described rather well by one common curve if the sum of the surface concentrations of adsorbed hydrogen and oxygen is plotted along the abscissa. This curve means that H$_2$ adsorption terminates when the sum of the surface concentrations of adsorbed hydrogen and oxygen is a constant independent of the individual surface concentrations of these gases. Such a form of the dependence of the differential molar heats of adsorption means that H-atoms are in competition with O-atoms for identical surface centers. It is known that the $d^8s^2 \rightarrow d^8s$ transition in Ni-atoms requires about 2.5 kJ/mol only. At the temperature of these experiments (463 K), this value is less than the thermal energy (3.84 kJ/mol). Obviously, in the nickel oxide matrix, the reduced Ni-atoms are capable of interacting with O-atoms in the $d^8s^2$ state or with H-atoms in the $d^8s$ state, as these states are easily interconvertible. Thus, the Ni-atoms are the adsorption sites for hydrogen and oxygen chemisorption.

In Section 3.1., we have shown that modernizations of the adsorption and calorimetric techniques and procedures lead to the conclusion that neither geometric nor induced heterogeneity of the surfaces reveals itself in the heats of chemisorption and catalytic activities measured on metal powders. The molar heats of chemisorption are constant or almost constant in a wide range of surface coverage and fall near the surface saturation. The following two figures show that the same tendency can be traced for adsorption on metal films and filaments under ultra-vacuum conditions. Figure 10 presents the data on the molar heats of H$_2$ adsorption measured on evaporated Ni-films at 293–298 K. These data were published by different authors in 1950–1966. It is seen that, with time, the molar heats of adsorption over the range of moderate coverages decrease (evidently, as a consequence of killing out the side processes) and the coverage dependence comes to zero. Similarly to the data presented in Figure 4, the higher the numbers of the calendar years, the lower and the closer to the horizontal line the curves over the region of moderate coverages.

![Figure 10. Hydrogen adsorption on evaporated nickel films at 293–298 K under ultra-vacuum conditions: 1 - [99], 1950; 2 - [100], 1953; 3 - [101], 1960; 4 - [102], 1964, and 5 - [103], 1966](image-url)
measurements led to the molar heats of H₂ adsorption coverage-independent over a wide range of surface coverages. These data confirm the tendency noted in Section 3.1. and illustrated by Figures 4 and 10.

The results of measurements of the molar heats of chemisorption of gases on metals allow the conclusion that modernizations of the adsorption and calorimetric techniques and procedures for ultra-vacuum and high-vacuum measurements went synchronously.

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