The nature, kinetics, and ultimate storage capacity of hydrogen sorption by carbon nanostructures

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DOI: 10.1070/PU2006v049n06ABEH002424

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<u>Abstract.</u> The review covers the present state of studies of the urgent open questions concerning the nature, kinetics, and limit values of hydrogen sorption by carbon nanostructures. These questions are related to the key issues in the problem of building a hydrogen electrical automobile. Considered are the thermo-dynamic and diffusion characteristics and the micromechanisms of the processes of chemical and physical sorption of hydrogen by graphite and related carbon nanomaterials, and also the various methodological aspects of studying and optimizing such hydrogen adsorbents. The experimental and theoretical prerequisites and prospects for developing a 'superadsorbent' (≥ 10 mass %) for storing hydrogen onboard an automobile are also discussed.

1. Introduction

The depletion of energy resources and environmental pollution, being the key issues closely related to the constant development of society, require immediate solution [1]. In this connection, hydrogen is considered an ideal fuel because

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Received 24 January 2005, revised 30 January 2006 Uspekhi Fizicheskikh Nauk **176** (6) 581–610 (2006) Translated by E Yankovsky; edited by A M Semikhatov it is ecologically clean, abundant, and renewable (in the sense of virtually unlimited natural resources and regeneration capacity) [2]. Safe and low-cost storage and transportation of hydrogen are the key elements of the hydrogen power industry [2].

The central issue of generating energy from hydrogen for an ecologically clean automobile is related to the need of creating effective techniques for storing and using hydrogen in a car, which is formulated, for instance, in the US National Project for the period up to 2015 for the development of systems and materials (sorbents) for the compact storage of hydrogen onboard an automobile [3-5].

During the last decade, new carbon nanomaterials, such as single-wall and multiwall carbon nanotubes and graphite nanofibers (GNFs) (Figs 1 and 2), were considered promising sorbents of hydrogen for automobile fuel cells by many researchers and were intensively studied (see the reviews in Refs [6–11]). In many studies between 1997 and 2005 [6–11], the important open questions about the nature, mechanisms, and ultimate storage capacity of hydrogen sorption by carbon nanostructures (single-wall nanotubes, multiwall nanotubes, GNFs, etc.) and the prospects for using such nanostructures as material for the hydrogen power industry were studied to a certain extent.

The reviews show that numerous experimental data obtained in various laboratories in 1997-2002 (Figs 3 and 4) and 2002-2005 [8–11] on the sorption capacity for hydrogen by the new carbon nanomaterials have a spread of about three orders of magnitude, that the most interesting experimental results are not reproducible in other laboratories, and that no experimental explanation or justification of such a situation exists.



Figure 1. Schematic design and micrographs of carbon nanostructures: (a) GNF, (b) multiwall nanotubes, and (c) a bundle of single-wall nanotubes.



Figure 2. Sorption of hydrogen by a bundle of single-wall nanotubes: *I*, inside nanotubes, the theoretical value of the binding energy (physical adsorption) -0.062 eV ($-6.0 \text{ kJ} \text{ mol}^{-1}(\text{H}_2)$); *2*, in channels between nanotubes (-0.119 eV, $-11.5 \text{ kJ} \text{ mol}^{-1}(\text{H}_2)$); *3*, in surface grooves (-0.089eV, $-8.6 \text{ kJ} \text{ mol}^{-1}(\text{H}_2)$); *4*, on the outer surface of the bundle (-0.049 eV, $-4.7 \text{ kJ} \text{ mol}^{-1}(\text{H}_2)$).

In the well-known analytical work (2001) devoted to the study of the past, present, and future of storing hydrogen onboard an automobile in carbon nanomaterials, Dillon and Heben [6] stressed that a technological solution to this problem requires further and deeper studies of the fundamental aspects (mechanisms and characteristics) of the hydrogen – graphite interaction.

In a series of frequently cited works of 1995–1999 [12] done under the guidance of Rodriguez and Becker (whose anomalous results have not yet been reproduced or funda-



Figure 3. Data on the sorption capacity of GNF and oriented nanotubes extracted by volumetric (\bullet), gravimetric (\blacktriangle), and electrochemical (\blacktriangledown) methods; RT stands for 'room temperature.'



Figure 4. Data on the sorption capacity of bundles of single-wall nanotubes extracted by the volumetric (\bullet), gravimetric (\blacktriangle), and electrochemical (\blacktriangledown) methods; RT stands for 'room temperature.'

mentally justified or disproved by anyone, including the authors of these 'know-how' works [13]), it was announced that a GNF-based superadsorbent with the sorption capacity up to 40-60 mass% at 300 K and hydrogen pressure 11 MPa had been fabricated (see Fig. 3, Chambers et al.). This situation was thoroughly discussed by Maeland in a 2002 review published in Ref [7], where fundamental aspects requiring further study were also noted.

There are grounds to believe [3-11] that in the last four to five years, despite the numerous studies based on the best theoretical and experimental methods, little has changed in this 'uncomfortable' situation (see Figs 3 and 4) and its diagnosis discussed in the reviews of 2001 and 2002 [6, 7] in relation to revealing the nature, mechanisms, and characteristics of the interaction of hydrogen with carbon nanomaterials. This was also noted in the analytical reviews of 2004 and 2005 [10, 11], where the conclusion is drawn (tantamount to the same diagnosis of the situation) that further fundamental studies are needed; otherwise, no effective solution to the existing technological problems is possible. On the other hand, during the last few years, especially in the period from 2001 to 2003, interest in carbon nanomaterials as adsorbents for hydrogen fuel has waned in a number of Western European countries, Japan, and Russia (see the 2003 reviews in [8, 14, 15]). Apparently, the reason lies in the abovementioned irreproducibility, in the large spread of the experimental data on the sorption capacity of these materials, and, in particular, in the sharply negative experimental results of 2001 [16] that so far have not been confirmed by the majority of researchers (see Figs 3 and 4, Tibbetts et al.).

At the same time, in 2004, the US Department of Energy announced [3-5] that US \$150,000,000 had been allocated for establishing three new Centers of Excellence for fundamental research into materials for hydrogen storage (with a view to manufacture hydrogen-driven vehicles), including the DOE National Center for Carbon Hydrogen Storage at the National Renewable Energy Laboratory (NREL), with the goal of achieving a breakthrough in overcoming the principal technical barriers in the field of onboard hydrogen storage. The plan is [3-5] by the end of the 2006 fiscal year to come to a final decision on the continuation or termination of financing such research in the field of carbon nanomaterials. The decision will depend on the results in the reproducibility of the given sorption capacity (6 mass% hydrogen) at technologically achievable temperatures and pressures of hydrogen saturation.

All this suggests that we are, to a certain extent, at a critical, decisive point as regards the prospects of using carbon nanomaterials as hydrogen sorbents for automobile fuel cells. Obviously, solving this problem requires the use of novel concepts and methods.

In a series of papers written in 2003–2005, the present author, together with collaborators, examined novel concepts and methods and used them to solve some of the urgent problems on the basis of the thermodynamic analysis, systematization, and comparison of the experimental and theoretical data. This work is given special attention in the present analytical review.

2. Some important open questions concerning the nature, mechanisms, and characteristics of hydrogen sorption by carbon nanostructures

The US Department of Energy formulated goals [3-5] to develop, by 2010, hydrogen adsorbents with a high sorption capacity (≤ 6 mass% of hydrogen, H/C ≥ 0.77 , and 45 grams of hydrogen per liter) and a sufficiently fast kinetics (reversibility) of hydrogen desorption at room temperature. The authors (Dillon, Heben, and others) of the most frequently cited experimental work [26] on hydrogen sorption by surface structures consisting of bundles of single-wall nanotubes believe [27] that these goals can be achieved by using novel carbon nanostructures with anomalous values $(20-40 \text{ kJ mol}^{-1})$ of energies of hydrogen binding (bond rupture). These energy values are intermediate in relation to the well-known typical values of bond rupture energies for chemisorption and physical sorption of hydrogen by carbon materials. It is assumed [27] that (i) dissociative hydrogen adsorption on such carbon nanomaterials is characterized by the formation of bonds weaker than the typical chemical C-H bonds and (ii) nondissociative absorption is characterized by an interaction stronger than the physical sorption.¹ The

¹ The numbering of the processes corresponds to that adopted in Ref. [27].

authors of [27] relate the rapid removal of adsorbed hydrogen in process (i) to hydrogen spillover [28]; in the case of process (ii), they consider molecular adsorption of hydrogen on carbon nanomaterials subject to structural and/ or molecular modification.

The considered values of the binding energy of hydrogen and carbon materials $(20-40 \text{ kJ mol}^{-1}, [27])$ are roughly ten times higher than the binding energy (rupture of Van der Waals bonds) characteristic of physical adsorption of hydrogen on carbon materials [29-35] (Fig. 2 shows theoretical values [32]) and are approximately ten times lower than the energy of rupture of covalent C–H bonds characteristic of chemisorption [35-40].

In a series of experiments in [41], the manifestation of 'super' Van der Waals or weak chemical interaction of hydrogen with fullerites (C_{60} and $Na-C_{60}-H$) and carbon nanotubes was studied.

The authors of [42] noted the possibility of interpreting their data on measurements of the thermal electromotive force and electric resistivity of hydrogen-saturated single-wall nanotubes both within the model of physical sorption with an interaction stronger than the Van der Waals and in the model of chemisorption with an interaction weaker than that in typical covalent C-H bonds.

In a series of experimental studies of the mechanical synthesis of hydrogen with nanostructured graphite, Orimo et al. [14] also examined the manifestation of anomalous hydrogen–graphite sorption interaction weaker than in chemisorption but stronger than in physical sorption.

The possibility of 'chemilike' physical adsorption of hydrogen in carbon nanomaterials was discussed in theoretical paper [35].

At the same time, it must be noted that not a single researcher discussed the mechanisms of this weak chemical or 'superphysical' interaction. As was emphasized in [11], there is still no clear picture of the mechanism of hydrogen sorption by carbon nanotubes and nanofibers.

It is therefore reasonable to give a more detailed analysis of the conditions needed for manifestation and a meaningful interpretation of the anomalous values of the energy characteristics [27] in the sorption of hydrogen by carbon nanomaterials, and of the nature (chemisorption or physical sorption), mechanisms, the ultimate sorption capacity, and the diffusion kinetics of the sorption processes with these energy characteristics by using novel concepts, methods, and analytical results [10, 17-25].

3. Chemisorption of hydrogen in graphite and related carbon nanostructures

3.1 Methodological aspects

The methods in [10, 17-25] were primarily those of the thermodynamics of reversible processes and the linear approximation of the thermodynamics of irreversible processes (in a somewhat novel version), used to critically and constructively analyze and systematize a large body of experimental data on hydrogen sorption by graphite and new carbon nanomaterials (with sp² hybridization). The goal of this analysis was the experimental determination of the fundamental thermodynamic, transport, and diffusion characteristics of the relevant processes. In interpreting the obtained characteristics, in particular, we used the well-known results in [36] on first-principle calculations by the

MO method (*ab initio* MO) of the energies of chemisorption of atomic hydrogen by graphite and by carbon nanostructures.

This approach has been successfully used (see Refs [43–50]) to solve a number of related pressing problems involving the gas-solid interaction; to a certain extent, the results obtained there were used in [10, 17–25]. For instance, using the approach in [43] to analyze R Kirchheim's unique data and other data allowed us to expose new fundamental aspects of the micromechanisms of formation of hydride-like nanose-gregations on dislocations in palladium. In addition, using the approach in [47] to process the appropriate experimental data allowed us to substantially modify (for effects ranging from two to seven orders of magnitude) the widely used Lifshits–Slezov and Wagner theories of internal oxidation and coagulation of depositions in metals.

In the sections that follow, we examine the concepts and methods developed in Refs [10, 17-25], and the procedures and results of their application to the analysis and systematization of the most reliable experimental data on hydrogen sorption by carbon materials.

Section 4 describes a new method [7] used in thermaldesorption studies (temperature-programmed desorption, or TPD, TPD peaks, and TPD spectra) to experimentally determine the thermodynamic, diffusion, and transport characteristics of sorption processes and to establish their nature. In what follows, this method is used to analyze the experimental data.

3.2 Dissociative chemisorption of hydrogen

3.2.1 Process III². One of the processes similar to process (i) in Ref. [27] is the dissociative chemical adsorption of hydrogen (H_2^{gas}) (process III in Refs [10, 27]) in graphene layers in the crystal lattice of isotropic graphite [51, 53] (Figs 5 and 7a, TPD peak III) and related carbon nanostructures with sp² hybridization, including GNF (Fig. 6, TPD peak γ (III)) and nanostructured graphite [14, 52–56] (Figs 7b and c, TPD peak III).

Chemisorption process II, described by the overall reaction (4) below, can be related to the following reaction stages:

$$\frac{1}{2} H_2^{\text{gas}} \Leftrightarrow H^{\text{s}}, \qquad (1)$$

$$\mathbf{H}^{\mathrm{s}} \to \mathbf{H}^{\mathrm{l}}\,, \tag{2}$$

$$H^{l} + C^{ch} \Leftrightarrow (C - H)^{abs}, \qquad (3)$$

$$\frac{1}{2} H_2^{gas} + C^{ch} \Leftrightarrow (C - H)^{abs}, \qquad (4)$$

where H^s is atomic hydrogen on the surface of grains or graphite nanoregions of the material, H^1 are hydrogen atoms in the graphite lattice (between graphene layers) outside chemisorption centers, C^{ch} are internal carbon centers of chemisorption of hydrogen atoms in the graphene layers corresponding to potential C-H complexes, and $(C-H)^{abs}$ are the absorbed hydrogen atoms on carbon chemisorption centers in the graphene layers of the material (C-H complexes).

 2 Here and in what follows, the numbering of processes I – IV corresponds with that adopted in Refs [10, 17].



Figure 5. Temperature-programmed desorption curves (with TPD peaks I–IV) for deuterium from ISO-88 isotropic graphite hydrogen-saturated at 60 kPa (5 hours) at the temperatures 473 K (I), 673 K (2), 773 K (3), 973 K (4), and 1173 K (5) [5].



Figure 6. Temperature-programmed desorption curves (with TPD peaks β (I) and γ (III)) for hydrogen from GNF samples hydrogen-saturated at 298 K (24 hours) at the pressure 11 MPa (*I*) and 0.1 MPa (*2*). The dashed curves represent the peaks of curve (*I*) [12].

The analysis in Refs [10, 17] shows that in the first (dissociation) and third (chemical) stages of the overall process III, the state of the hydrogen-saturated material subjected to thermal-desorption heating is in many cases close to equilibrium (local equilibrium, or reversibility), and (1) and (3) are not limiting stages. The second stage, (2), may be diffusion-limited, i.e., the stage that determines the rate of the overall process III corresponding to the TPD peak III in experiments involving temperature-programmed desorption of hydrogen from the material.

Process III [reaction (4)] is characterized [10, 17] by the experimental value [51] of the standard enthalpy (heat) of the bulk solution, or the chemisorption of one mole of hydrogen atoms from the initial state H_2^{gas} in the graphite lattice of the material, $\Delta H_{(4)III} = -19 \pm 1$ kJ mol⁻¹(H), and the experimental value [51, 52, 54, 55] of the effective energy (enthalpy)



Figure 7. TPD spectra of deuterium and the fitting curves [53] for carbon materials: (a) ISO-88 isotropic graphite hydrogen-saturated in the course of 5 hours at 973 K and 60 kPa (see Fig. 5, curve 4); (b) ISO-88 isotropic graphite after irradiation by 20 keV ions of D₂ with the dose 5×10^{23} m⁻²; and (c) nanostructured graphite (mechanical synthesis with deuterium in a ball mill for 80 hours at 1 MPa and 300 K [14]).

of the bulk-diffusion activation of hydrogen atoms in the graphite lattice, $Q_{III} = 250 \pm 3 \text{ kJ mol}^{-1}(\text{H})$.

Taking the experimental data in [51] into account, we can write the mass action law for reaction (4) as [10, 17]

$$K_{(4)\rm III} = \frac{X_{\rm III}/X_{\rm IIIm}}{\left(P_{\rm H_2}/P_{\rm H_2}^0\right)^{1/2} \left[1 - \left(X_{\rm III}/X_{\rm IIIm}\right)\right]},$$
 (5)

which corresponds to the Sieverts–Langmuir absorption isotherm, i.e., the Langmuir dissociative absorption isotherm, which at small pressures $(K_{(4)III}(P_{H_2}/P_{H_2}^0)^{1/2} \ll 1)$ corresponds to the Sieverts isotherm

$$\frac{X_{\rm III}}{X_{\rm IIIm}} = \frac{K_{(4)\rm III} (P_{\rm H_2}/P_{\rm H_2}^0)^{1/2}}{1 + K_{(4)\rm III} (P_{\rm H_2}/P_{\rm H_2}^0)^{1/2}} \approx K_{(4)\rm III} \left(\frac{P_{\rm H_2}}{P_{\rm H_2}^0}\right)^{1/2}, \quad (5a)$$

where the equilibrium constant for reaction (4) is described by

$$K_{(4)\text{III}} = \exp\left(\frac{\Delta S_{(4)\text{III}}}{R}\right) \exp\left(-\frac{\Delta H_{(4)\text{III}}}{RT}\right) \tag{6}$$

with

$$\Delta H_{(4)\text{III}} \approx \frac{1}{2} \,\Delta H_{\text{dis}} + \Delta H_{(3)\text{III}} \,. \tag{7}$$

Here, X_{III} is the equilibrium concentration $(H/C^1)_{III}$ of the hydrogen atoms absorbed by the graphite lattice of the material at the pressure $P_{\rm H_2}$ (Pa) and temperature T (K), i.e., the ratio of the number of dissolved hydrogen atoms to the number of carbon atoms in the graphite lattice, which in some cases is close to the total number of carbon atoms in the material (C¹ \leq C); $X_{\text{IIIm}} = (\text{H/C}^1)_{\text{IIIm}} \leq 1.0$ is the maximum (carbohydride) concentration [10, 17, 57]; $P_{\text{H}_2}^0 = 1$ Pa is the standard hydrogen pressure; $\Delta S_{(4)III}$ is the standard entropy for reaction (4); R is the molar gas constant; $\Delta H_{\rm dis} = 448 \pm 2 \text{ kJ mol}^{-1}({\rm H}_2)$ is the experimental value [58] of the dissociation energy of one mole of gaseous hydrogen; $\Delta H_{\rm dis} = 448 \pm 2$ kJ mol(H) is the indirect experimental value (an estimate via formula (7) can be found in Refs [10, 17]) of the energy (enthalpy) of formation of chemical C-H bonds between hydrogen atoms and carbon centers in the graphene layers of the material (Fig. 8, with model F* corresponding to sp³ rehybridization [36, 37]); and $\Delta H_{(1)\text{III}} = 1/2 \Delta H_{\text{dis}}$, $\Delta H_{(2)\text{III}} \approx 0$, and $\Delta H_{(3)\text{III}}$ are the standard enthalpies for reactions (1)-(3) as applied to process III.

Using the model in [10, 43] for bulk diffusion of hydrogen atoms in the graphite lattice accompanied by reversible capture of the duffusant on internal chemisorption centers in graphene layers, we can write the effective diffusivity ($D_{\rm III}$) and the effective diffusion-activation enthalpy (energy) ($Q_{\rm III}$) as

$$D_{\rm III} \approx \frac{A_{\rm III} D^{\rm l}}{K_{(3)\rm III}} \,, \tag{8}$$

$$Q_{\rm III} \approx Q^{\rm l} - \Delta H_{\rm (3)III} \approx -\Delta H_{\rm (3)III} , \qquad (9)$$



Figure 8. Theoretical models of hydrogen atom chemisorption on graphite [36].

where $A_{\rm III} \approx \text{const}$, $K_{(3)\rm III}$ is the equilibrium constant for reaction (3) as applied to process III, and D^1 and Q^1 are the diffusivity and the diffusion activation energy for hydrogen atoms in the graphite lattice in the absence of chemisorption capture centers or at maximum (carbohydride) filling of these centers. Knowing the experimental values of $Q_{\rm III}$ and $\Delta H_{(3)\rm III}$, we can use Eqn (9) to obtain the indirect value $Q^1 = 7 \pm 4 \text{ kJ mol}^{-1}(\text{H}).$

The value of $\Delta H_{(3)III}$ obtained in [10, 17] from thermodynamic equations (5) and (9) and the experimental values of $\Delta H_{(4)\text{III}}$ and ΔH_{dis} [51, 58] can obviously be interpreted as the indirect experimental value, which is approximately half (in absolute value) the C-H binding energy in the methane molecule and the H-H binding energy in the hydrogen molecule $(-\Delta H_{\rm dis})$ [58]. However, the value of $\Delta H_{(3)\rm III}$ is close to the theoretical value of the energy of interaction (the energy of C-H bond formation) of hydrogen atoms and the graphene (cylindrical) surface of various single-wall nanotubes (50% filling) obtained by the density functional method (density functional theory, or DFT) [57]; it is also close to the experimental value [59] of the energy of formation of a C-H bond that links hydrogen atoms and carbon atoms in fullerene C₆₀ (with the filling factor H/C = 36/60), i.e., in a quasigraphene spherical layer.

The indirect experimental value of the binding energy $\Delta H_{(3)\text{III}}$ [10, 17] is much larger (by 8%, i.e., beyond the limits of experimental error) in absolute value than the energy of dissociation of half a mole of H₂ (1/2 ΔH_{dis}) [58], which explains the experimentally observed fact [51] that process III [reaction (4)] of dissolution (dissociative chemisorption) of hydrogen in the graphite lattice between graphene layers is exothermic. The desorption enthalpy (energy) $-\Delta H_{(4)\text{III}}$ is then close to the value of the energy characteristic of dissociative sorption process (i) in Ref. [27] and amounts to approximately 8% of the C–H bond rupture energy ($-\Delta H_{(3)\text{III}}$); the remaining 92% of that energy is provided by the energy of association of one mole of hydrogen atoms into molecules ($-1/2 \Delta H_{\text{dis}}$).

The thermodynamic characteristic $-\Delta H_{(3)\rm III}$ manifests itself almost entirely in the effective energy of bulk diffusion activation of hydrogen atoms in the graphite lattice ($Q_{\rm III} \approx -\Delta H_{(3)\rm III}$) spent mainly on the rupture of the C–H bond of the duffusant. The bulk diffusion of hydrogen atoms in the material is then accompanied by reversible capture [local equilibrium for reaction (3)] of the duffusant by chemisorption carbon centers in graphene layers, which results in the thermodynamic contribution $-\Delta H_{(3)\rm III}$ to $Q_{\rm III}$ being much larger than the negligible kinetic contribution Q^1 .

Thus, a characteristic feature of the dissociative chemisorption of hydrogen by carbon materials (process III) is the formation of (approximately 50%) weaker bonds than the typical chemical C-H bonds, e.g., in the methane molecule, and the desorption energy 19 kJ mol⁻¹ close to the value, discussed in [27], of the energy characteristic of process (i), which the authors of Ref. [27] identified with the energy of rupture of the hypothetical weak chemical C-H bond.

This, in particular, implies that to identify chemisorption process III (the TPD peak III) in a carbon material, we must experimentally determine the thermodynamic characteristics $\Delta H_{(4)\text{III}}$ and sorption equations (5), as well as the diffusion characteristics Q_{III} of the process (the appropriate method is described in Section 4).

Estimates based on Eqn (5a) show that by the order of magnitude, the equilibrium concentration $X_{\text{III}} = (\text{H}/\text{C}^1)_{\text{III}}$ of the dissolved hydrogen atoms in GNF and in nanostructured (in mechanical synthesis) graphite at 300 K and at the hydrogen pressure 1–10 MPa approaches 0.77, or 6 mass%. This value is defined in Refs [3–5] as the lower limit of the sorption capacity of adsorbent materials suitable for storing hydrogen in vehicles. The given estimate is confirmed by the analysis in [10, 17] of the sorption data in [12, 14, 54–56].

But the diffusion kinetics of the discharge of chemisorbed hydrogen from carbon materials at room temperature (process III) does not meet the technological requirements [3-5] for hydrogen-driven vehicles, mainly because of the high value of the hydrogen-diffusion activation energy $Q_{\rm III}$.

There is one aspect that should be mentioned in concluding this subsection. The indirect experimental value of the energy (enthalpy) of formation of a chemical C-H bond linking hydrogen atoms to carbon centers in graphene layers of the material ($\Delta H_{(3)III} = -243 \pm 3 \text{ kJ mol}^{-1}(\text{H})$) is determined independently from the experimental values of $\Delta H_{(4)III}$ and $\Delta H_{\rm dis}$ via Eqn (7) and from the experimental values of $Q_{\rm III}$ and Q^1 [in accordance with Eqn (9)]. The value of $\Delta H_{(3)III}$ thus obtained is close to the experimental value -255 ± 1 kJ mol⁻¹(H) [59] of the enthalpy of formation of a C-H bond in the fullerene hydride $C_{60}H_{36}$ (i.e., the filling of a quasigraphene spherical layer is H/C = 36/60) and to the theoretical values $-(220 - 260) \pm 20 \text{ kJ mol}^{-1}(\text{H})$ of the energy of formation of a C-H bond linking hydrogen atoms to the graphene (cylindrical) surface of various singlewall nanotubes with the filling factor H/C = 0.5 obtained in [57] by the density functional method. At the same time, the experimental value of $\Delta H_{(3)III}$ agrees only in order of magnitude with the theoretical value $-194 \text{ kJ mol}^{-1}(\text{H})$ [36] (calculations were done by the ab initio MO method by computing the energies of chemisorption of atomic hydrogen by graphite) corresponding to the assumed model (F* in Fig. 8) of chemisorption process III. The same situation occurs when the experimental value of $\Delta H_{(3)III}$ is compared [10] with a series of theoretical (DFT) values, which, as shown in [38], may be essentially because 'collective stabilization' of chemisorbed hydrogen on graphene surfaces was ignored.

3.2.2 Process IV. Much higher absolute values of the energy characteristics of sorption, diffusion, and interaction of hydrogen with carbon materials, including isotropic [51, 53] (see Fig. 5, TPD peak IV), pyrolytic [60], and nanostructured [52, 53] (Fig. 7c, TPD peak IV) graphite, manifest themselves in another process of dissociative chemisorption of hydrogen discussed in Refs [10, 17] [process IV, reactions (1)-(4)], which occurs in defective regions of graphite structures. Chemisorption occurs at carbon centers, or ruptured C-C σ -bonds in 'chairlike' and/or 'zigzag' edge positions (see Fig. 8, models C and/or D, sp² hybridization) located in defective regions of the graphite lattice (C_{def}^{1}) . The experimental value [10, 17] of the energy (enthalpy) of formation of C-H bonds linking hydrogen atoms to such chemisorption centers [reaction (3)] is $\Delta H_{(3)IV} = -364 \pm 5 \text{ kJ mol}^{-1}(\text{H})$. Process IV [overall reaction (4)] is characterized [10, 17] by the experimental value [60] of the standard enthalpy of dissolution in the defective regions of the graphite lattice of one mole of hydrogen atoms (from the initial state of the molecular gas) $\Delta H_{(4)IV} \approx 1/2 \Delta H_{dis} + \Delta H_{(3)IV} = -140 \pm 5 \text{ kJ mol}^{-1}(\text{H})$ and by the effective energy (enthalpy) of the hydrogen-atom

diffusion activation in the same regions of the material, $Q_{\rm IV} \approx -\Delta H_{(3)\rm IV} = 365 \pm 50 \text{ kJ} \text{ mol}^{-1}(\text{H})$ [52, 60]. The characteristics of the process and of the corresponding TPD peak IV are described by equations similar to (5)–(9).

We note that the indirect experimental value $\Delta H_{(3)IV} = -364 \pm 5$ kJ mol⁻¹(H) is determined (corrected) using the experimental values of $\Delta H_{(4)IV}$ and ΔH_{dis} or the values of Q_{IV} and Q^1 via Eqns (7) and (9). The value of $\Delta H_{(3)IV}$ thus obtained agrees satisfactorily with the theoretical values -357 kJ mol⁻¹(H) and -378 kJ mol⁻¹(H) [36] (*ab initio* MO calculations) corresponding to the assumed models (C and/or D in Fig. 8) of chemisorption process IV.

3.3 Dissociative – associative chemisorption of hydrogen: a new concept

3.3.1 Process II. One of the sorption processes similar to nondissociative adsorption process (ii) in Ref. [27] is the dissociative – associative, or formally nondissociative, chemical adsorption of hydrogen (process II) from the initial state of the molecular gas (H_2^{gas}) into intergranular or defective (surface) regions in isotropic graphite [51, 53] (see Figs 5 and 7a, TPD peak II) and related carbon nanostructures, including GNF [12] (TPD peak β (II) in Fig. 6), nanostructured graphite [14, 53, 54] (TPD peak II in Figs 7b and c), single-wall nanotubes deformed in a ball mill [61] (see Fig. 4, Hirscher et al.), and defective multiwall nanotubes [62].

Chemisorption process II [overall reaction (13)] can be related (see Refs [10, 17]) to the reaction stages

$$\mathbf{H}_2^{\mathrm{gas}} \to \mathbf{H}_2^{\mathrm{def}}\,,\tag{10}$$

$$\mathbf{H}_{2}^{\mathrm{def}} \Leftrightarrow 2\mathbf{H}^{\mathrm{def}},\tag{11}$$

$$2\mathrm{H}^{\mathrm{def}} + \mathrm{C}^{\mathrm{def}}_{\mathrm{ch}} \Leftrightarrow (\mathrm{C} = 2\mathrm{H})^{\mathrm{def}}_{\mathrm{ch}} \,, \tag{12}$$

$$H_2^{gas} + C_{ch}^{def} \rightarrow (C = 2H)_{ch}^{def}, \qquad (13)$$

where H_2^{def} and H^{def} are hydrogen molecules or atoms in the respective intergranular or defective regions of the material (C^{def}) outside the carbon chemisorption centers and (C = 2H)_{ch}^{def} denotes adsorbed pairs of hydrogen atoms on carbon chemisorption centers or ruptured C–C σ -bonds in zigzag edge positions (see Fig. 8, model H, sp³ hybridization) localized in intergranular or defective regions of the material.

As in the case of process III, the analysis in Refs [10, 17] shows that at the dissociation (11) and chemical (12) stages of overall process II, the state of the hydrogen-saturated material subjected to thermal-desorption heating is in many cases close to equilibrium (local equilibrium, or reversibility), which means that these are not limiting stages. The first stage, reaction (10), may be diffusion-limited, i.e., determining the rate of the overall process (13) corresponding to the TPD peak II.

Process II is characterized (see Refs [10, 17]) by the standard enthalpy (heat) of the chemisorption of one mole of hydrogen molecules from the initial state of the molecular gas H_2^{gas} in intergranular or defective regions of the material, $\Delta H_{(13)II} \approx -110 \text{ kJ mol}^{-1}(\text{H})$ (indirect experimental and theoretical estimates) and by the experimental value [51, 54, 61, 62] of the effective energy (enthalpy) of bulk diffusion activation of hydrogen molecules in these regions, $Q_{II} = 120 \pm 2 \text{ kJ mol}^{-1}(\text{H}_2)$.

The mass action law for reaction (13) can be written as [10, 17]

$$K_{(13)II} = \frac{X_{II}/X_{IIm}}{(P_{H_2}/P_{H_2}^0)(1 - X_{II}/X_{IIm})},$$
(14)

which corresponds to the Henry–Langmuir isotherm, i.e., the Langmuir nondissociative adsorption isotherm (the Fermi–Dirac distribution), which at small pressures $(K_{(13)II}(P_{H_2}/P_{H_2}^0) \ll 1)$ corresponds to the Henry isotherm

$$\frac{X_{\rm II}}{X_{\rm IIm}} = \frac{K_{(13)\rm II}(P_{\rm H_2}/P_{\rm H_2}^0)}{1 + K_{(13)\rm II}(P_{\rm H_2}/P_{\rm H_2}^0)} \approx K_{(13)\rm II} \frac{P_{\rm H_2}}{P_{\rm H_2}^0} \,. \tag{14a}$$

The equilibrium constant for reaction (13) is described by the formula

$$K_{(13)\text{II}} = \exp\left(\frac{\Delta S_{(13)\text{II}}}{R}\right) \exp\left(-\frac{\Delta H_{(13)\text{II}}}{RT}\right),\tag{15}$$

$$\Delta H_{(13)\Pi} = \Delta H_{(10)\Pi} + \Delta H_{(11)\Pi} + \Delta H_{(12)\Pi}$$

$$\approx \Delta H_{\rm dis} + \Delta H_{(12)\Pi} , \qquad (16)$$

where $X_{\rm II}$ is the equilibrium concentration $({\rm H}_2/{\rm C}^{\rm def})_{\rm II}$ of adsorbed hydrogen molecules in intergranular or defective regions of the carbon material (C^{def}) at the pressure $P_{\rm H_2}$ (Pa) and temperature T (K), i.e., the ratio of the number of adsorbate molecules to (H₂) the number of carbon atoms in the intergranular or defective regions of the material (C^{def} \ge C^{def}_{ch}), which may be close to the number of sorption centers C^{def}_{ch}; $X_{\rm IIm} = ({\rm H}_2/{\rm C}^{\rm def})_{\rm IIm} \le 0.5$ is the maximum (carbohydride) local concentration of the adsorbate; $\Delta S_{(13)\rm II}$ is the standard entropy for reaction (13); and $\Delta H_{(12)\rm II} = -560 \pm 10 \text{ kJ mol}^{-1}(2\text{H})$ is the experimental value of the molar energy (enthalpy) of formation of the chemical bond (C=2H) that links two hydrogen atoms to a carbon center in a zigzag edge position (Fig. 8, model H) localized in intergranular or defective (surface) regions of the carbon material.

Using the model in [10, 17] for the diffusion of hydrogen molecules in the graphite lattice accompanied by reversible dissociation and capture of the duffusant on carbon chemisorption centers, we express the effective diffusivity ($D_{\rm II}$) and the effective diffusion-activation enthalpy (energy) ($Q_{\rm II}$) as

$$D_{\rm II} \approx \frac{A_{\rm II} D^{\rm def}}{K_{(11)\rm II} K_{(12)\rm II}} \approx \frac{A_{\rm II} D^{\rm def}}{K_{(13)\rm II}} , \qquad (17)$$

$$Q_{\mathrm{II}} \approx Q^{\mathrm{def}} - (\Delta H_{(11)\mathrm{II}} + \Delta H_{(12)\mathrm{II}}) \approx -\Delta H_{(13)\mathrm{II}}, \qquad (18)$$

where $A_{\rm II} \approx \text{const}$; D^{def} and Q^{def} are the diffusivity and the diffusion-activation energy of hydrogen molecules in the intergranular or defective regions of the carbon material in the absence of chemisorption capture centers or at the maximum (carbohydride) filling of these centers; $Q^{\text{def}} \approx 10 \pm 5 \text{ kJ mol}^{-1}(\text{H}_2)$ (experimental and theoretical estimates [10, 17]); $K_{(11)\text{II}}$ and $K_{(12)\text{II}}$ are the equilibrium constants for reactions (11) and (12); and $\Delta H_{(10)\text{II}} \approx 0$, $\Delta H_{(11)\text{II}} \approx \Delta H_{\text{dis}}$, and $\Delta H_{(12)\text{II}}$ are the standard enthalpies for reactions (10) – (12).

The desorption energy $-\Delta H_{(13)II}$ and the effective hydrogen-molecule diffusion activation energy Q_{II} represent only about 20% of the chemical bond rupture energy $-\Delta H_{(12)II}$. The dominant part (~ 80%) of the energy of rupture of chemical bonds linking hydrogen with chemisorption centers $(-\Delta H_{(12)II})$ comes from the energy of association of hydrogen atoms into molecules $(-\Delta H_{dis})$.

Therefore, TPD peak II (reaction (13)) corresponds to the diffusion of hydrogen molecules in intergranular and/or defective (surface) regions of the carbon material accompanied by reversible dissociation and capture of the diffusant on chemisorption C=2H centers [the local equilibrium for reactions (11) and (12)]. We note once more that with such a mechanism of process II, only about 20% of the chemical-bond rupture energy $-\Delta H_{(12)II}$ contributes to the energy characteristics of hydrogen desorption and diffusion, $-\Delta H_{(13)II}$ and Q_{II} .

The values of the energy characteristics $-\Delta H_{(13)II}$ and Q_{II} for process II, which is formally described by the Henry– Langmuir isotherm for nondissociative adsorption [Eqns (14) and (14a)], is several times greater than the value of the energy characteristic for process (ii) (20–40 kJ mol⁻¹), which is discussed in [27] and is identified with the energy of rupture of hypothetical 'superphysical' bonds.

The energy of chemical bond rupture per mole of hydrogen atoms in process II is given by $-1/2 \Delta H_{(12)II} \approx$ $280 \text{ kJ mol}^{-1}(\text{H})$, which corresponds to an intermediate value if we compare it with similar characteristics $-\Delta H_{(3)III} \approx$ $243 \text{ kJ mol}^{-1}(\text{H})$ and $-\Delta H_{(3)IV} \approx 364 \text{ kJ mol}^{-1}(\text{H})$ for the respective processes III and IV.

Estimates based on Eqns (14) and (15) suggest that the equilibrium (local) concentration of adsorbed hydrogen molecules in the intergranular nanoregions in GNFs and nanostructured graphite at 300 K and a hydrogen pressure 1-10 MPa is close in the order of magnitude to the carbohydride value $(H_2/C^{def})_{IIm} \approx 0.5$. In other words, the hydrogen content in the material may approach the value [3-5] that makes such materials suitable for use as adsorbents for hydrogen-driven vehicles; this agrees with the results in [10, 17] of processing the sorption data in [12, 14, 54–56]. At the same time, for process II (as well as for processes III and IV), the rate of diffusion discharge of chemisorbed hydrogen from the material at room temperature is low (basically because of the high value of Q_{II}), which does not meet the technical requirements [3–5] for hydrogen-driven vehicles.

There is one aspect that should be mentioned in concluding this subsection. The indirect experimental value $\Delta H_{(12)II} = -560 \pm 10 \text{ kJ mol}^{-1}(2\text{H})$ is determined (including the correction and matching of all the involved quantities) either from the experimental values of $\Delta H_{(13)II}$ and ΔH_{dis} [Eqn (16)] or from Q_{II} , ΔH_{dis} , and Q^{def} [Eqn (18)]. The value of $\Delta H_{(12)II}$ obtained this way agrees satisfactorily with the theoretical value $-540 \text{ kJ mol}^{-1}(2\text{H})$ [36] (*ab initio* MO calculations) corresponding to the proposed models (H in Fig. 8) of the chemisorption process IV and is also comparable to the theoretical value $-476 \text{ kJ mol}^{-1}(2\text{H})$ [36] in accordance with model G in Fig. 8.

3.3.2 Process I. Another process discussed in Refs [10, 17] that very closely resembles the nondissociative adsorption process (ii) in Ref. [27] in terms of the values of energy characteristics is the dissociative–associative, or formally nondissociative, chemical adsorption of hydrogen from the initial state H_2^{gas} on the surface of isotropic graphite pellets [51, 53] (see Fig. 5, TPD peak I) and carbon nanostructures, single-wall nanotubes [26, 63, 64], and multiwall nanotubes [62].

Chemisorption process I corresponds (similarly to process II) to overall reaction (13) with stages (10)-(12) for which surface areas of the material should be considered

instead of defective or intergranular regions of localization of sorption centers. For process I, the chemisorption centers of two hydrogen atoms are, apparently, the ruptured C–C σ -bonds in the chair-like edge carbon (monatomic) positions (model G in Fig. 8) and/or alternating carbon (diatomic) positions in a graphene layer (see Fig. 8, model F, sp³ rehybridization). Reaction (12) is then applicable only to chair-like edge carbon monatomic centers (C^s_{ch}) corresponding to model G. For diatomic carbon centers corresponding to model F, instead of a stage similar to (12), we must consider the reaction

$$2\mathrm{H}^{\mathrm{s}} + \mathrm{C}^{\mathrm{s}}_{2\mathrm{ch}} \Leftrightarrow (\mathrm{C}_2 = 2\mathrm{H})^{\mathrm{s}}_{\mathrm{ch}}, \qquad (12\mathrm{a})$$

where H^s are hydrogen atoms in surface areas of the material (C^s) outside the diatomic carbon chemisorption centers (C^s_{2ch}) and (C₂ = 2H)^s_{ch} are adsorbed pairs of hydrogen atoms at the diatomic carbon centers localized on the surface of the material.

Process I is described by expressions similar to (14)-(18) and is characterized [10, 17] by the experimental value [31, 51] (Section 5.1) of the standard enthalpy (heat) of adsorption of one mole of hydrogen molecules,

$$\Delta H_{(13)I} \approx \Delta H_{\text{dis}} + \Delta H_{(12)I} \approx \Delta H_{\text{dis}} + \Delta H_{(12a)I}$$

= -10 ± 7 kJ mol⁻¹(H₂),

where $\Delta H_{(12)I} \approx \Delta H_{(12a)I} = -460 \pm 10 \text{ kJ mol}^{-1}(2\text{H})$ is the experimental value of the energy (enthalpy) of formation of C = 2H chemical bonds linking two hydrogen atoms to one carbon atom or the C₂ = 2H bonds linking two hydrogen atoms to two carbon atoms on the surface of the adsorbent (see Fig. 8, models G and F, respectively).

Process I is characterized [10, 17] by the experimental value [26, 62–64] of the effective energy (enthalpy) of the hydrogen-molecule diffusion activation $Q_{\rm I} \approx Q^{\rm s} - \Delta H_{(13)\rm I} = 20 \pm 2 \text{ kJ mol}^{-1}(\rm H_2)$, where $Q^{\rm s} = 10 \pm 8 \text{ kJ mol}^{-1}(\rm H_2)$ is the experimental value of the energy of hydrogen-molecule diffusion activation on the surface of the material or at the maximum (carbohydride) filling of the chemisorption centers of diffusant capture.

We believe (see Refs [10, 17]) that $Q^{s} \approx Q^{def} \sim 10 \text{ kJ mol}^{-1}(\text{H}_2)$ and that such values of the energy of the hydrogen-molecule diffusion activation in carbon materials occur in the process of nondissociative physical sorption of hydrogen.

We also note [10, 17] that the experimental values of the diffusion (transport) characteristics Q^s , Q^{def} , and Q^1 (Sections 3.2 and 3.3.1) agree quite well (in the order of magnitude) with the values of the energy of activation hydrogen diffusion in nanostructured graphite obtained in NMR studies [65]. Apparently, this corresponds to the conditions needed for the hydrogen–graphite Van der Waals interaction to emerge and also agrees with the theoretical values in [40, 66, 67] for the diffusion characteristics calculated without taking the effect of chemisorption centers of diffusant capture into account.

The desorption energy $(-\Delta H_{(13)I})$ and the effective diffusion-activation energy (Q_I) of hydrogen molecules for process I represent only a small fraction of the rupture energy $-\Delta H_{(12,12a)I}$ for bonds linking hydrogen to chemisorption centers. The greater part of the rupture energy comes from the energy $-\Delta H_{dis}$ of hydrogen-atom association into molecules.

Therefore, process I is the diffusion of hydrogen molecules in surface nanolayers of the carbon material accom-

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panied by reversible dissociation and capture of the diffusant at chemisorption centers [local equilibrium for reactions (11), (12), and (12a)]. With such a mechanism for process I, a small fraction (several percentage points) of the chemical-bond rupture energy $-\Delta H_{(12,12a)I}$ manifests itself in the energy characteristics of the hydrogen desorption and diffusion, $-\Delta H_{(13)I}$ and Q_I .

The values of the energy characteristics of hydrogen desorption and diffusion for process I, which, similarly to process II, is described by the Henry–Langmuir isotherm for nondissociative absorption (14a), are comparatively close to the energy value 20-40 kJ mol⁻¹ for process (ii) discussed in [27] and identified with the energy of rupture of 'superphysical' bonds.

The molar energy of chemical-bond rupture for process I per hydrogen atom is given by $-1/2 \Delta H_{(12,12a)I} \approx 230 \text{ kJ mol}^{-1}(\text{H})$, which corresponds to the smallest value when comparing it with similar characteristics $(-1/2 \Delta H_{(12)II}, -\Delta H_{(3)III}, \text{ and } -\Delta H_{(3)IV})$ for processes II, III, and IV.

The analysis of the experimental data performed in [10, 17] and in Sections 5.1 and 5.2 shows that process I in singlewall and multiwall nanotubes at technological pressures and temperatures of hydrogen saturation can ensure a high local (surface) concentration of the adsorbed hydrogen, close in the order of magnitude to the carbohydride value, and also an acceptable (by the requirements formulated in Refs [3-5]) rate of the diffusion discharge of chemisorbed hydrogen from the material at room temperature (because of the low value of Q_1). It was also found that process I may be interpreted as chemisorption whose energy characteristics are relatively close to those needed for physical sorption to occur (to a certain extent, this is a 'physical-like' chemisorption).

In concluding this subsection, we note that the indirect experimental value $\Delta H_{(12)I} \approx \Delta H_{(12a)I} = -460 \pm$ 10 kJ mol⁻¹(2H) can be found either from the experimental values of $\Delta H_{(13)I}$ and ΔH_{dis} or from the values of Q_I , ΔH_{dis} , and Q^{s} [using the appropriate equation (16) or (18) for process I]. The experimental value of $\Delta H_{(12, 12a)I}$ satisfactorily agrees with the theoretical values -476 kJ mol⁻¹(2H) and $-389 \text{ kJ} \text{ mol}^{-1}(2\text{H})$ [36] corresponding to the assumed models G and/or F in Fig. 8 of chemisorption process I. In considering the value -389 kJ mol⁻¹(2H) [36], which corresponds to model F, the possibility, mentioned in Section 3.2.1, of a systematic underrating of theoretical results due to ignoring the 'collective stabilization' of chemisorbed hydrogen on graphene surfaces must be taken into account [38]. In interpreting type-I sorption processes, we must allow for the possibility of using other models, e.g., those described in Refs [35-40].

3.4 Characteristics and some manifestations of chemisorption processes I-IV

The various characteristics and mechanisms of hydrogen chemisorption in graphite and related carbon nanomaterials with sp^2 hybridization corresponding to processes I–IV are listed in Table 1.

Processes III and II in carbon nanomaterials manifest themselves in the IR spectra (process II), in the proton NMR spectra, in the nature of neutron diffraction, in the X-ray absorption spectra, and also (process III) in a substantial increase in the interplanar spacing for graphene layers (see the review articles in Refs [9, 10]). Process II is also characterized by an accompanying (initiated by the process) occurrence of a fairly small amount of hydrocarbons (CH₄ and others) in thermal desorption spectra. The explanation of this phenomenon is (see Ref. [10]) that the energy $-\Delta H_{(12)II}$ of desorption (detachment) of two hydrogen atoms from the carbon atom of the sorption center is much higher than the energy $-\Delta H_{C-C} \approx 485 \text{ kJ mol}^{-1}$ of detachment of a carbon atom from the two nearest carbon neighbors (see Fig. 8, model H).

The value of the enthalpy of the formation of a C–C σ -bond (sp² hybridization) in graphite (ΔH_{C-C}) was estimated in Ref. [10] by the well-known formula $\Delta H_{C-C} \approx -(2/z_C) \Delta H_C$ [68], where ΔH_C is the graphite sublimation enthalpy [58] and $z_C = 3$ is the coordination number in a graphene layer. Reasoning in a similar way, we can estimate the enthalpy of the formation of a C–C σ -bond (sp³ hybridization) in diamond as -357 kJ mol⁻¹ at $z_C = 4$.

The above investigation showed that the effective energy of desorption and diffusion-activation of hydrogen molecules for process I ($-\Delta H_{(13)I}$ and Q_I) amounts to a few percentage points of the energy of the rupture of chemical bonds, $\Delta H_{(12,12a)I}$. If we ignore the dissociative–associative (internal) mechanism, the overall process I, similarly to process II, formally (at the beginning and the end) manifests itself as a nondissociative adsorption of hydrogen molecules by carbon materials (type-(ii) process in Ref. [27]). The values of the effective energy characteristics of process I ($-\Delta H_{(13)I}$ and Q_I) can be considered intermediate when compared [27] with the known values of interaction (bond rupture) energies characteristic of the chemical [35–40] and physical [29–35] adsorption of hydrogen by carbon structures.

There are reasons to believe (see Refs [10, 36-38, 69]) that the effective energy characteristics of the desorption and diffusion of hydrogen for type-I processes may be very close to the typical values of the interaction energy for physical sorption. We note in this connection that in isotropic graphite [51, 53], two TPD peaks occur whose characteristics are close; apparently, the peaks are of type I (see Fig. 5, desorption curve *I*) and may also occur in carbon nanostructures.

We note that in the case of a nondissipative physical adsorption of hydrogen molecules by carbon materials [29-35, 69], there are no internal dissociative-associative and chemical stages (11), (12), and (12a) that are characteristic of formally nondissociative chemisorption of hydrogen molecules (processes I and II).

There is also the insufficiently explored factor of the catalytic effect [27, 28, 55] of metallic nanoparticles, soot, and amorphous carbon that are present in carbon materials at the dissociative stages in chemisorption processes I-IV at room temperatures and lower. Obviously, this is not a decisive factor in physical adsorption.

In Section 4, we describe a novel method for processing TPD spectra (a modified Kissinger method) that allows identifying the nature of nondissociative adsorption processes, i.e., distinguishing between type-I chemisorption processes and the processes of physical adsorption, with close energy characteristics of diffusion and sorption.

4. Some aspects of determining sorption characteristics from temperature-programmed desorption spectra. Identifying the nature of sorption

In a number of studies (e.g., see Refs [26, 54, 61-64, 70]) of the temperature-programmed desorption of hydrogen from carbon nanomaterials, the researchers determined the deso-

Hydrogen chemisorption in sp ² carbon materials	Chemisorption and diffusion models and the energies of formation of chemical bonds link- ing the hydrogen atoms to the material	Characteristics of the processes	Type of sorption isotherm		
Process III in isotropic graphite [51, 53] (Figs 5 and 7a, TPD peak III), in GNFs [12] (Fig. 6, peak γ (III)), and in nanostructured graphite [14, 52–56] (Figs 7b and c, III)	Dissociative chemisorption of hydrogen be- tween graphene layers [reactions (1)—(4)]. Bulk diffusion of hydrogen atoms with a reversible diffusant capture at chemisorption centers in graphene layers (Fig. 8, model F*); $\Delta H_{(3) \Pi} = -243 \pm 3 \text{ kJ mol}^{-1}(\text{H})$	$\begin{split} \Delta H_{(4)\mathrm{III}} &\approx 1/2 \Delta H_{\mathrm{dis}} + \Delta H_{(3)\mathrm{III}} \\ &\approx -19 \pm 1 \mathrm{kJ} \mathrm{mol}^{-1}(\mathrm{H}), \\ \Delta S_{(4)\mathrm{III}}/R &\approx -14.7 (-15.4) \\ \mathrm{at} X_{\mathrm{m}} &\approx 0.5 (1.0), \\ \mathrm{Eqns} (5) - (7). \\ D_{\mathrm{III}} &= D_{\mathrm{0III}} \exp(-Q_{\mathrm{III}}/RT), \\ D_{0\mathrm{III}} &\approx 3 \times 10^{-3} \mathrm{cm}^2 \mathrm{s}^{-1}, \\ Q_{\mathrm{III}} &\approx Q^1 - \Delta H_{(3)\mathrm{III}} \\ &\approx 250 \pm 3 \mathrm{kJ} \mathrm{mol}^{-1}(\mathrm{H}), \\ Q^1 &\approx 7 \pm 4 \mathrm{kJ} \mathrm{mol}^{-1}(\mathrm{H}), \\ \mathrm{Eqns} (8), (9) \end{split}$	Sieverts – Langmuir Equations (5), (5a)		
Process II in isotropic graphite [51, 53] (Figs 5 and 7a, II), in GNFs [12] [Fig. 6, peak β (II)], in nanostruc- tured graphite [53, 54] (Figs 7b and c, peak II), and in defective single- wall [61] and multiwall [62] nano- tubes	Dissociative–associative chemisorption of H ₂ in intergranular or defective (surface) regions [reactions (10)–(13)]. Diffusion of H ₂ in these regions with reversible diffusant dissociation and capture at sorption centers (Fig. 8, model H); $\Delta H_{(12) II} \approx -560 \pm 10 \text{ kJ mol}^{-1}(2\text{H})$	$ \begin{split} \Delta H_{(13)\mathrm{II}} &\approx \Delta H_{\mathrm{dis}} + \Delta H_{(12)\mathrm{II}} \\ &\approx -110 \ \mathrm{kJ} \ \mathrm{mol}^{-1}(\mathrm{H}_2), \\ \Delta S_{(13)\mathrm{II}}/R &\approx -30 \\ \mathrm{at} \ X_{\mathrm{IIm}} &\approx 0.5 \ (0.25), \\ \mathrm{Eqns} \ (14) - (16). \\ D_{\mathrm{II}} &= D_{0\mathrm{II}} \ \mathrm{exp} (-Q_{\mathrm{II}}/RT), \\ D_{0\mathrm{II}} &\approx 1.8 \times 10^3 \ \mathrm{cm}^2 \ \mathrm{s}^{-1}, \\ Q_{\mathrm{II}} &\approx 2^{\mathrm{def}} - \Delta H_{(13)\mathrm{II}} \\ &\approx 120 \pm 2 \ \mathrm{kJ} \ \mathrm{mol}^{-1}(\mathrm{H}_2), \\ Q^{\mathrm{def}} &\approx 10 \pm 5 \ \mathrm{kJ} \ \mathrm{mol}^{-1}(\mathrm{H}_2), \\ \mathrm{Eqns}(17), \ (18) \end{split} $	Henry – Langmuir Equations (14), (14a)		
Process I in isotropic graphite [51, 53] (Fig. 5, TPD peak I), in single-wall nanotubes [26, 63, 64], and in multiwall nanotubes [62] (Section 5.1)	Dissociative–associative chemisorption of H ₂ in surface layers of the material [reactions (10)–(13) and (12a)]. Diffusion of H ₂ in these layers with reversible diffusant dissociation and capture at chemi- sorption centers (Fig. 8, models G and F); $\Delta H_{(12,12a)1} \approx -460 \pm 10 \text{ kJ mol}^{-1}(2\text{H})$	$ \begin{split} \Delta H_{(13)1} &\approx \Delta H_{\rm dis} + \Delta H_{(12,12a)1} \\ &\approx -10 \pm 7 \ \rm kJ \ mol^{-1}(H_2), \\ \Delta S_{(13)1}/R &\approx -20 \ \rm at \ X_{\rm Im} &\approx 0.5 \\ (0.25), \ \rm Eqns \ of \ the \ (14) - (16). \\ D_1 &= D_{01} \exp(-Q_1/RT), \\ D_{01} &\approx 3 \times 10^{-3} \ \rm cm^2 \ s^{-1}, \\ Q_1 &\approx Q^{\rm s} - \Delta H_{(13)1} \\ &\approx 20 \pm 2 \ \rm kJ \ mol^{-1}(H_2), \\ Q^{\rm s} &\approx 10 \pm 8 \ \rm kJ \ mol^{-1}(H_2), \\ Eqns \ (17), \ (18) \end{split} $	Henry – Langmuir Equations (14), (14a)		
Process IV in isotropic [51, 53] (Fig. 5, peak IV) and in pyrolytic [60] and nanostructured [52, 53] (Fig. 7a, peak IV) graphite	Dissociative chemisorption of H ₂ in defective regions of the graphite lattice [reactions (1)– (4)]. Bulk diffusion of hydrogen atoms in defective regions with reversible diffusant capture by chemisorption centers (Fig. 8, models C and D); $\Delta H_{(3)}$ IV $\approx -364 \pm 5$ kJ mol ⁻¹ (H)	$ \begin{aligned} \Delta H_{(4)\text{IV}} &\approx 1/2 \Delta H_{\text{dis}} + \Delta H_{(3)\text{IV}} \\ &\approx -140 \pm 5 \text{ kJ mol}^{-1}(\text{H}), \\ \text{Eqns}(5) - (7). \\ D_{\text{IV}} &= D_{0\text{IV}} \exp(-Q_{\text{IV}}/RT), \\ D_{0\text{IV}} &\approx 6 \times 10^2 \text{ cm}^2 \text{ s}^{-1}, \\ Q_{\text{IV}} &\approx -\Delta H_{(3)\text{IV}} \\ &\approx 365 \pm 50 \text{ kJ mol}^{-1}(\text{H}), \\ \text{Eqns}(8), (9) \end{aligned} $	Sieverts – Langmuir Equations (5), (5a)		
Note. D _{0III} , D _{0I} , and D _{0IV} are the pre-exponential (entropic) factors of hydrogen diffusivities (D _{III} , D _I , and D _{IV}) for carbon materials					

Table 1. Characteristics of hydrogen chemisorption and diffusion in isotropic graphite and related carbon nanostructures.

corresponding to the respective processes.

rption activation energy (E_a^{des}) from the dependence of the temperature T_m of the TPD peak maximum on the material heating rate β using the Kissinger method (Figs 9 and 10). They assumed that the process was a first-order reaction, for which the Polanyi–Wigner transport equation yields the expression [70]

$$\ln\frac{T_{\rm m}^2}{\beta} = \frac{E_{\rm a}^{\rm des}}{RT_{\rm m}} + B\,,\tag{19}$$

where R is the molar gas constant and B is a dimensionless constant omitted in a similar expression (1) in Ref. [70] and described in Eqn (24) below.

The value of E_a^{des} was determined (see Refs [26, 54, 61-64, 70]) from a diagram (Fig. 9c and the inset in Fig. 10) representing the linear dependence of $\ln(T_m^2/\beta)$ on $1/T_m$ (the Kissinger coordinates). The resulting transport characteristic $-E_a^{\text{des}}$ was identified [63, 70] with the thermodynamic

characteristic ΔH^{ads} , the heat of adsorption of hydrogen by the material.

In this connection, it seems logical to examine and substantiate the method of using TPD spectra to determine the diffusion (or transport) characteristics of hydrogen sorption by carbon materials for chemisorption processes I-IV (Table 1 in particular).

In the case where the limiting stage of the thermal desorption process is the diffusion removal of hydrogen from the material heated in a vacuum at the constant rate $\beta = \partial T/\partial t$, the process may be formally regarded as a first-order reaction with the hydrogen desorption rate described by the equation [68, 71]

$$v(t) = -\frac{\partial X(t)}{\partial t} = K(T(t)) X(t), \qquad (20)$$

where X(t) is the average concentration of the diffusant adsorbate remaining in the material subjected to desorption



Figure 9. The results in [26] of measuring the thermal desorption of hydrogen from carbon materials. (a) TPD spectrum (peak A) of the initial hydrogen-saturated single-wall nanotube sample (1) and hydrogen-saturated activated carbon (2) (×10 magnification); TPD spectra (peaks A and B) of a single-wall nanotube sample annealed (prior to hydrogen saturation) in a vacuum at 970 K (3). (b) TPD spectra (peaks B) saturated with hydrogen for 10 minutes at 273 K and 3 minutes at pressures ranging from 3.3 to 40 kPa, which corresponds to surface fillings (θ) ranging from 0.3 to ~ 1. (c) The dependence (in Kissinger coordinates) of the TPD peak maximum B on the rate of heating of single-wall nanotubes.

heating, K(T(t)) is the desorption rate constant at the material temperature T(t) corresponding to the heating time t, and $1/K = \tau$ is the relaxation time of the process, i.e., the time during which 63% of the adsorbate leaves the material:

$$K(T(t)) = K_0 \exp\left(-\frac{Q}{RT(t)}\right), \qquad (21)$$

$$K_0 = \frac{1}{\tau_0} \approx \frac{D_0}{L^2} \,, \tag{22}$$

where K_0 and T_0 are the pre-exponential factors of the rate constant and the relaxation time of the diffusion process of hydrogen desorption from the material [68, 71], Q and D_0 are the effective diffusion-activation energy and the pre-exponential factor of the diffusivity of hydrogen in the material (Table 1), and L is the characteristic diffusion length (the path length) for the process of removal of hydrogen from the material [68, 71].

The condition for the maximum desorption rate at T_m , $\partial v/\partial T = 0$, yields the sought expressions

$$\frac{T_{\rm m}^2}{\beta} = \frac{Q}{RK(T_{\rm m})} \approx \frac{QL^2}{RD(T_{\rm m})} , \qquad (23)$$

$$\ln\left(\frac{T_{\rm m}^2}{\beta}\right) = \frac{Q}{RT_{\rm m}} + \ln\left(\frac{Q}{RK_0}\right),\tag{24}$$

where $K(T_m)$ and $D(T_m)$ are the rate constant and the diffusivity at T_m .

We note that Eqn (23) in the general kinetic setting, i.e., without (22) being substituted into it, is similar to Eqn (1) in Ref. [63], which contains a misprint, an 'inverted' factor R/E_a^{des} in the right-hand side. Equations (23) and (24) can be used in analyzing the TPD spectra in order to determine the diffusion characteristics of sorption processes, including processes I–IV.

It is also possible to estimate L using the formula [10, 18]

$$L \approx \left(\frac{D(T_{\rm m})\,\Delta T}{\beta}\right)^{1/2},$$
 (25)

where ΔT is the half-height width of the TPD peak.

To confirm the diffusion nature of the limiting stage of the process, we must study the dependence of the temperature $T_{\rm m}$ of the maximum of the TPD peak on *L* for a given material heating rate β , i.e., we must study the value of the intercept $2\ln(QL/RD_0)$ on the Kissinger vertical axis (see Fig. 9c and the inset in Fig. 10) as a function of *L* on the diagram representing the linear dependence of $\ln(T_{\rm m}^2/\beta)$ on $1/T_{\rm m}$, Eqn (24). In particular, in studying chemisorption processes I or II, it is advisable to carry out TPD experiments with samples of various thicknesses, because diffusion removal of the adsorbate to the free surface of the samples may be the limiting factor, i.e., the thickness of the sample (the smallest linear size) may be given by the characteristic diffusion path *L* [10, 18].

In the case where the desorption of hydrogen is limited not by the stage of diffusion removal of the adsorbate but by the 'chemical' kinetic stage, the rate constant K(T(t)) in Eqns (20)–(24) and the pre-exponential (frequency, or entropy) factor K_0 are described by the Polanyi–Wigner transport equation [70]; it is then advisable to use the kinetic characteristic E_a^{des} instead of Q. We note that in most cases, the typical values of K_0 for different chemical reactions are not lower than 10^9 s^{-1} (in the order of magnitude) [68, 70], which simplifies the identification of the nature of the process.

The difference in the adsorption and desorption activation energies (E_a^{ads} and E_a^{des} , respectively) is the enthalpy, or heat, of the sorption process [68],

$$\Delta H^{\rm ads} = E_{\rm a}^{\rm ads} - E_{\rm a}^{\rm des} \,, \tag{26}$$

provided that the direct and 'inverse' reactions follow the same path. In the typical case where $E_a^{ads} = 0$, we have



Figure 10. The results in [70] of measuring the TPD spectra (peaks A and B) for hydrogen in single-wall nanotube samples that were hydrogen-saturated for 1 hour at 298 K and 2 MPa. Different TPD curves correspond to different heating rates (β , K min⁻¹). The inset shows the dependence (in Kissinger coordinates) of the TPD peak maximum A on the heating rate of the sample.

 $\Delta H^{\rm ads} = -E_{\rm a}^{\rm des}$, which has been used by many researchers (e.g., see Refs [63, 70]).

It is also advisable to examine a possible method for estimating the activation energy E_a^{des} of sorption processes by using the TPD spectra of the sample with a single heating rate β that ensures a sufficient 'spread' of the processes in temperature and time.

This novel but simple and efficient method (compared with the Kissinger method) can be illustrated, e.g., by curve *3* (peaks A and B) in Fig. 9a, which can be described (up to a constant 'scaling' factor) by the equation

$$\frac{\partial X_{\rm A}}{\partial T} + \frac{\partial X_{\rm B}}{\partial T} = -\frac{1}{\beta} \left[K_{\rm A} X_{\rm A} (T(t)) + K_{\rm B} X_{\rm B} (T(t)) \right], \quad (27)$$

where

$$K_{\rm A}(T(t)) = K_{0\rm A} \exp\left(-\frac{E_{\rm A}}{RT}\right),$$

$$K_{\rm B}(T(t)) = K_{0\rm B} \exp\left(-\frac{E_{\rm B}}{RT}\right)$$

are the rate constants, $X_A(T(t))$ and $X_B(T(t))$ are the running values of the adsorbate concentration in the heated sample for different temperatures T(t), and E_A and E_B are the activation energies (E_a^{des}) of the respective desorption processes. In the case of diffusion kinetics, E_A and E_B correspond to the respective diffusion-adsorbate activation energies.

After the TPD peaks A and B (curve 3 in Fig. 9a) have been separated and the areas $S_A(T(t))$, $S_A(T(t \to \infty)) \approx S_{\infty A}$, $S_{\infty B}$, and $S_B(T(t))$ of the peaks are determined for different temperatures T(t), we can estimate the relative adsorbate concentrations corresponding to different temperatures and the respective heating times using the expressions

$$\frac{X_{\rm A}(T(t))}{X_{0\rm A}} = \frac{S_{\infty\rm A} - S_{\rm A}(T(t))}{S_{\infty\rm A}},$$
(28)

$$\frac{X_{\rm B}(T(t))}{X_{\rm 0B}} = \frac{S_{\rm \infty B} - S_{\rm B}(T(t))}{S_{\rm \infty B}},$$
(29)

where X_{0A} and X_{0B} are the initial concentrations of the adsorbed hydrogen at t = 0.

Next, we can determine the desorption activation energies of the processes A and B using the formulas

$$\ln\left\{\frac{\partial X_{A}/\partial T}{\left[S_{\infty A}-S_{A}(T(t))\right]/S_{\infty A}}\right\} = -\frac{E_{A}}{RT} + \text{const}, \quad (30)$$

$$\ln\left\{\frac{\partial X_{\rm B}/\partial T}{\left[S_{\infty \rm B}-S_{\rm B}(T(t))\right]/S_{\infty \rm B}}\right\} = -\frac{E_{\rm B}}{RT} + {\rm const}\,.$$
(31)

Estimating the desorption activation energies for processes corresponding to the TPD peaks A and B (curve 3 in Fig. 9a) from Eqns (27)–(31) yields values $E_A \approx E_B \approx Q_I$ close to the diffusion activation energy Q_I for chemisorption process I (Table 1). This agrees with the results in [26, 27], where the Kissinger method was used to analyze the thermal desorption data. The corresponding results are given in Section 5.1 (Table 2).

Similar estimates for TPD peaks for isotropic graphite [51, 53] (see Figs 5 and 7a), for irradiated isotropic graphite [53] (Fig. 7b), and for nanostructured (by mechanical synthesis with hydrogen) graphite [14, 53] (Fig. 7c) yield values of $E_{\rm a}^{\rm des}$ close to those of $Q_{\rm II}$, $Q_{\rm III}$, and $Q_{\rm IV}$ in Table 1. Reasoning in a similar manner, we can obtain values of $E_{\rm A}^{\rm des}$ for the TPD peaks β and γ for GNF samples [12] (see Fig. 6) that are close to $Q_{\rm II}$ and $Q_{\rm III}$, respectively. The same method can be used for the complex processing and comparison of gravimetric (integral) and TPD (differential) data presented, e.g., in Ref. [12].

Based on expressions of type (5), (6), (14), and (15), the thermodynamic characteristics of a sorption process, including ΔH^{ads} , can be determined from experiments that study the dependence of the area of a TPD peak on the temperature and pressure of the hydrogen-saturated material, controlling the way in which the equilibrium state is reached [10, 51].

The total equilibrium concentration $X_{\Sigma} = (H/C)_{\Sigma}$ of the hydrogen absorbed by the carbon material (at the hydrogen

Parameter	TPD peak A		TPD peak B	
	[70], Fig. 10	[26]; Fig. 9a, curve 3	[70], Fig. 10	[26], Fig. 9
$E_{\mathrm{a}}^{\mathrm{des}},$ kJ mol ⁻¹ (H ₂)	$19.2 \pm 1.2 \ (\approx Q_{\rm I}, {\rm Table \ 1})$ Equation (24)	20 Equations (27)–(31)	20 Equation (24)	19.6 Equation (24)
K_0,s^{-1}	$\begin{array}{c} (1\pm0.2)\times10^9\\ Equation~(24) \end{array}$	$\begin{array}{c} 2.5\times10^6\\ \text{Equation (24)} \end{array}$	5.7×10^2 Equation (24)	1.8×10^2 Equation (24)
<i>L</i> , μm	0.015 Equations (22), (23), (25)	0.3 Equations (22), (23), (25)	80 Equations (22), (23), (25)	40 – 70 Equations (22), (23), (25)
$D(T_{\mathrm{m}}),\mathrm{cm}^{2}\mathrm{s}^{-1}$	4 × 10 ⁻⁷ (100 K) Equation (25)	5×10^{-7} (148 K) Equation (25)	$\sim D_{\rm I}(T_{\rm m})$ Equation (25)	$\sim D_{\rm I}(T_{\rm m})$ Equation (25)
$D_{\mathrm{I}}(T_{\mathrm{m}}),\mathrm{cm}^{2}\mathrm{s}^{-1}$	$1 \times 10^{-13} (100 \text{ K})$ Table 1	$2.6 \times 10^{-10} (148 \text{ K})$ Table 1	_	
$D^{\rm s}(T_{\rm m}),{\rm cm}^2{ m s}^{-1}$	$4 \times 10^{-7} (100 \text{ K})$	$2 \times 10^{-5} (148 \text{ K})$	_	—
	(при $D_0^{\rm s} \approx 7 \times 10^{-2} { m cm}^2 { m s}^{-1}$ и ў	$Q^{s} \approx 10 \text{ kJ mol}^{-1}(\text{H}_{2}), \text{ Table 1})$		
$\Delta H^{ m ads} \ \Delta S^{ m ads}$				$ \sim \Delta H_{(13)1} \\ \sim \Delta S_{(13)1} \\ \text{Equations (14), (15)} \\ \text{for process I, Table 1} $
$X = H_2/C$ $X_m = (H_2/C)_m$	$X_{\rm A} \ge X_{\rm B}$	$X_{\rm A} \ge X_{\rm B}$	$X_{\rm B} \leqslant X_{\rm A}$	$\begin{array}{c} X_{\rm B} \leqslant X_{\rm A} \\ \sim 0.3 \!-\! 0.7^{*} \end{array}$
* The experimental (abso 10 mass%, $\sim 0.3-0.7$), at	blute) values [26] of hydrogen sorpt re overvalued (systematic error) by	ion corresponding to peaks A and apparently a factor of 10.	B, including the maximum	n values for peak B ($\sim 5-$

 Table 2. TPD data on single-wall nanotube samples

saturation temperature T and pressure P_{H_2}), which corresponds to chemisorption processes I–IV, can be described by the equation [10, 17]

$$X_{\Sigma} \approx 2\left(\frac{C^{s}}{C}\right)X_{I} + 2\left(\frac{C^{def}}{C}\right)X_{II} + \left(\frac{C^{l}}{C}\right)X_{III} + \left(\frac{C^{l}_{def}}{C}\right)X_{IV}, \qquad (32)$$

in which the atomic fractions (the factors in parentheses) of the localization regions of the different chemisorption centers in the material are taken into account.

The methods by which the atomic fractions of the surface sorption-active regions and the maximum local concentrations of the adsorbent are indirectly determined through experiments and the way in which the nature of the process is identified are discussed and illustrated by examples in the next section, where we analyze the results in Refs [26, 62-64, 70, 72].

5. The use of novel approaches in analyzing sorption data

5.1 A method for determining the fraction of surface carbon atoms and active sorption centers in single-wall nanotubes. The sorption-monolayer model

We examine the widely cited data [26] (see Fig. 4, Dillon et al., and Fig. 9) on the TPD peaks A and B for single-wall nanotube samples (0.1-0.2 mass%) with a predominant content of soot and amorphous carbon (~ 80 mass%) and a metallic catalytic agent (~ 20 mass% Co). It must be noted that nobody has so far been able to reproduce these data. Hydrogen saturation was done for 10 minutes at 273 K and a hydrogen pressure up to 40 kPa with subsequent ageing and additional hydrogen saturation for 3 minutes at 133 K. The experimental value of the thermal adsorption activation energy [$E_a^{des} \approx 19.6$ kJ mol⁻¹, Eqn (19)] obtained in [26] for the TPD peak B (Fig. 9c) coincides with the value of Q_I in Table 1. It is therefore useful to examine the possibility of interpreting the data in Ref. [26] by employing the characteristics of dissociative–associative hydrogen chemisorption (process I, Table 1) and using the method described in Section 4.

Using the experimental dependence [26] of $T_{\rm m}$ of peak B on β (Fig. 9c) and formula (24), we can estimate that K_0 amounts to approximately $2 \times 10^2 \, {\rm s}^{-1}$, which is obviously not a typical value of the frequency factor ($K_0 \ge 10^9 \, {\rm s}^{-1}$) of the rate constant in the Polanyi–Wigner transport equation for chemical reactions [68, 70]. Hence, we may assume that it is not the kinetic (chemical) but the diffusion stage that is the limiting stage in the process. Using the 'diffusion' expression (22) for K_0 and taking $D_{0\rm I}$ from Table 1, we obtain $L \sim 40 \, \mu$ m, which is obviously the total thickness of singlewall nanotube samples [26]. A close value $L \sim 70 \, \mu$ m is obtained (see Ref. [10]) if we use Eqn (25).

This implies that thermal desorption (peak B) from single-wall nanotube samples [26] is limited by hydrogen diffusion to their external surface, which formally manifests itself as a first-order reaction. The characteristic diffusion path L then corresponds to the total thickness of the samples, and the diffusivity is described by the equation and the characteristics D_{0I} , Q_I , and D_I for chemisorption process I (Table 1).

The absolute values of the concentration of hydrogen absorbed by nanotubes (~ 5–10 mass%, or $X = H_2/C \sim$ 0.3–0.7) at 133 K and 40 kPa given in Ref. [26] for the TPD peak B correspond to the maximum (carbohydride) concentration of the adsorbate ($X_{\rm Im} \approx 0.5$, Table 1) on all external and internal (graphene) surfaces of single-wall nanotube samples, in which theoretically [9, 29] almost all carbon atoms are at the surface ($C \approx C^{\rm s}$). In the sorption monolayer, obviously, there then exists no place for the adsorbate corresponding to TPD peak A, whose sorption capacity is of the same order as that for peak B (this follows from a comparison of the areas below the peaks in Fig. 9a).

In this connection we emphasize that the theoretical value of the total (inner and outer) specific surface area of individual nanotubes or their bundles $(S_{\text{tot}}^{\text{th}} \approx 2.6 \times$ $10^3 \text{ m}^2 \text{ g}^{-1}$) may be considered the upper limit for carbonbased materials only if the graphene levels do not have a high concentration of vacancies, nanononcontinuities, holes, or other defects [9, 29]. In his review in Ref. [9], Eletskii noted that because a single-wall nanotube is a surface structure, its entire mass is contained in the surface of its layers. In other words [29], the percentage of the surface carbon atoms in bundles of single-wall nanotubes may reach $\sim 100\%,$ i.e., $C \approx C^{s}$. Such an approach, however, does not account for the difference in the sorption activity of different sections of external and internal surfaces of the adsorbent (see Fig. 2) and the fact that the adsorbent molecules may reach these surfaces. Each carbon atom in a defect-free graphene layer of a single-wall nanotube contributes to the external and internal surfaces of the tube $(S_{\text{ext}}^{\text{th}} \approx S_{\text{int}}^{\text{th}} \approx 1.3 \times 10^3 \text{ m}^2 \text{ g}^{-1}$ [29]). We can assume that the presence of defects in graphene tubular layers allows carbon atoms from the defective areas to make an additional contribution to the specific surface area of the material. This is corroborated by the data in Eletskii's review [29], which provides experimental data on the specific surface areas for activated carbon (S^{exp}) exceeding S_{tot}^{th} for single-wall nanotubes by 15-27%. Such an excess may be caused by a high concentration of defects in the carbon samples and/or systematic errors inherent in the common method of determining S^{exp} from the Brunauer-Emmett-Teller (BET) adsorption isotherm for N₂ at 77 K. At the same time, the experimental values of the specific surface area of single-wall nanotubes are usually much (severalfold) smaller than the theoretical value S_{tot}^{th} [9, 29], which may be due to the differences in the surface activity and in the extent to which the adsorbate reaches different areas of the external and internal surfaces of the adsorbent (see Fig. 2). The fraction of the surface carbon atoms corresponding to the experimental value of the specific surface area of bundles of open single-wall nanotubes, whose internal surfaces can be reached by the adsorbate, can be estimated (by the order of magnitude) as

$$\gamma_{\exp}^{s} \approx \frac{C_{\exp}^{s}}{C} \approx \frac{S^{\exp}}{S_{tot}^{th}}$$
 (33)

For closed samples of single-wall nanotubes, we must obviously use $S_{\text{ext}}^{\text{th}}$ instead of $E_{\text{tot}}^{\text{th}}$ in Eqn (33).

As noted in a number of works (e.g., see Ref. [70]), the high absolute values (~ 5-10 mass%, $X = \text{H}_2/\text{C} \sim 0.3-0.7$) of hydrogen sorption by single-wall nanotubes [26] at fairly low pressures and temperatures of hydrogen saturation have not been confirmed by other researchers, which may be due to the difficulty (systematic errors) of accounting for and/or separating different effects because minute samples of the material, containing only ~ 0.1-0.2 mass% of single-wall nanotubes, were used in [26].

It may be assumed that to a much lesser degree, such systematic errors are compensated for by the use of relative adsorbate concentrations $\theta = X/X_{\rm m}$, with the maximum (carbohydride) adsorbate concentration $X_{\rm m} \sim 0.3-0.7$. We therefore believe that it is logically reasonable to consider the data in [26] on the pressure dependence of the adsorbate relative concentration, i.e., the data on the increase in the extent to which the sorption centers on the surface of the samples of single-wall nanotubes are filled with hydrogen molecules or, in other words, the increase in the filling factor θ from 0.3 to 0.1 as the hydrogen pressure grows from roughly 3.3 to 40 kPa (Fig. 9b).

As the surface filling factor increases, the position of the TPD peak B in Fig. 9b at $\beta \approx 1$ K s⁻¹ shifts from $T_m \approx 307$ K to $T_m \approx 276$ K at $\theta \approx 0.3$ and $\theta \sim 1$, respectively. According to Eqns (23) and (24), this corresponds to a decrease in the activation energy $Q \approx Q_I \approx Q^s - \Delta H_{(13)I}$ of the process by approximately 1 kJ mol⁻¹(H₂). This apparently indicates that the dependence of $\Delta H_{(13)I}$ and, therefore, of $\Delta H_{(12a)I}$ [Eqn (18) as applied to process I] on θ for the sorption centers on the surface of single-wall nanotubes is weak.

Using the data in Fig. 9b on the dependence of the monolayer filling factor $\theta = X/X_{\rm m}$ on the hydrogen pressure and Eqn (14) (as applied to process I), we can determine the equilibrium constant *K* of the hydrogen saturation of single-wall nanotube samples [26] at T = 133 K. If we then substitute the result in Eqn (15) and assume the adsorption enthalpy $\Delta H^{\rm ads} \approx \Delta H_{(13)\rm I}$ (Table 1) and T = 133 K, we obtain the adsorption entropy value $\Delta S^{\rm ads} \approx -17.5 R$, which is close (in the order of magnitude) to $\Delta S_{(13)\rm I}$ from Table 1.

Thus, the study of the data on single-wall nanotubes [26] shows that a type-I physical-like chemisorption process may occur in them.

Thermal desorption studies of single-wall nanotube samples (12–15 mass%, the rest being soot, amorphous carbon, and a metallic catalyst) with the mass about 100 mg, saturated with hydrogen for 2 hours at 298 K and 2 MPa and cooled to 77 K, with evacuation of the residual gas, were conducted in [70]. The Kissinger method was used to determine the hydrogen desorption activation energy $E_a^{des} = 19.2 \pm 1.2$ kJ mol⁻¹(H₂), which is close to Q_I (Table 1), and the pre-exponential factor of the rate constant $K_0 = (1 \pm 0.2) \times 10^9$ s⁻¹, Eqn (24), for the process corresponding to the TPD peak A in Fig. 10.

The TPD peak A was also observed in samples of multiwall nanotubes and activated carbon, which were saturated with hydrogen in a similar way [70]. We note that in single-wall and multiwall nanotubes, in contrast to activated carbon [70], TPD peak B appears in addition to peak A (see Fig. 10).

We recall that TPD peak A (Fig. 9a), as well as peak B, was also observed in [26] in single-wall nanotube samples and in activated carbon, where there was no peak B. Estimates (see Section 4) from Eqns (27)–(31) of the desorption activation energies for processes corresponding to TPD peaks A and B in single-wall nanotubes [26] yielded values of $E_A \approx E_B \approx Q_I$ close to the diffusion activation energy Q_I for chemisorption process I (Table 1). We believe it is useful to analyze the data of the TPD measurements for single-wall nanotubes in detail.

Analysis of the data in Table 2 suggests that it is acceptable to interpret TPD peak B in single-wall nanotubes [26, 70] as the manifestation of a physical-like chemisorption process of type I. It has been shown that thermal adsorption (peak B) from single-wall nanotube samples [26, 70] is limited by hydrogen diffusion to their external surface, which formally manifests itself as a first-order reaction. The characteristic diffusion path $L_{\rm B}$ for peak B (Table 2) corresponds to the total thickness of the samples, while the diffusivity is described by the equation and characteristics $(D_{0\rm I}, Q_{\rm I}, \text{ and } D_{\rm I})$ corresponding to chemisorption process I (Table 1).

As for the TPD peak A in single-wall nanotube samples [26, 70], there can be two interpretations: as a physical-like chemisorption process of type I (Table 1) or as a chemilike physical adsorption. In the first interpretation, thermal desorption (peak A) for single-wall nanotubes [26, 70] is limited by diffusion (a first-order reaction) of hydrogen from the inner regions of the bundles of single-wall nanotubes (and/or from the inner regions of individual nanotubes) to the interbundle, or interface, surfaces (and/or to the outer surfaces of the nanotubes). Obviously, the characteristic size $L_{\rm A}$ for peak A (Table 2) corresponds to the cross-sectional size (diameter) of the bundle (see Figs 1 and 2) or the distance to the closest exit from a nanotube, while the diffusivity is described by the equation and characteristics $(D_{0I}, O_{I}, and D_{I})$ corresponding to chemisorption process I. The process of the subsequent diffusion mass transfer of hydrogen (A) to the outer surface of single-wall nanotube samples, i.e., hydrogen transfer over distances of the order of $L_{\rm B}$ (Table 2), is then not limiting because it proceeds with a much higher diffusivity D^s (Table 2) characteristic of the Van der Waals interaction, i.e., of physical sorption. We may also assume that the chemisorption centers on outer surfaces, the interfaces of bundles or the outer surfaces of nanotubes, are not decelerating traps for the hydrogen diffusing to the outer surface of single-wall nanotubes (hydrogen A), because in the given conditions they are filled by hydrogen B to the limit, i.e., are 'frozen.' We note that with this interpretation of the data in [26] and [70], the adsorbed hydrogen corresponding to TPD peak A, i.e., hydrogen A, is localized primarily in the inner regions of single-wall nanotube bunches and/or in the inner regions (surfaces) of individual nanotubes, while hydrogen B is localized on the outer surfaces of bundles or nanotubes.

In the other interpretation of the data in Refs [26, 70], the thermal desorption of hydrogen (peak A) from single-wall nanotubes and from samples of activated carbon (Fig. 9a) is limited not by diffusion but by physical desorption (a firstorder reaction) with the activation energy $E_{\rm a}^{\rm des} =$ 19.2 ± 1.2 kJ mol⁻¹(H₂) and the pre-exponential (frequency, or entropy) factor of the rate constant in the Polanyi-Wigner transport equation [70] $K_0 = (1 \pm 0.2) \times 10^9 \text{ s}^{-1}$. Using Eqn (26), we obtain the experimental value of the enthalpy physical $\Delta H^{\mathrm{ads}} = -E_{\mathrm{a}}^{\mathrm{des}} =$ (heat) of adsorption -19.2 ± 1.2 kJ mol⁻¹(H₂), which agrees (in the order of magnitude) with some theoretical estimates (modified DFT) [69] of the Van der Waals interaction energy.

The above discussion shows that the physical nature and the energy characteristics $\Delta H^{ads} = -E_a^{des}$ of the sorption process corresponding to TPD peak A may be close to those of chemisorption process I, i.e., may correspond to a chemilike physical adsorption of hydrogen. At the same time, process A, as well as sorption processes corresponding to TPD peak B in single-wall nanotube samples [26, 70], may correspond to a physical-like chemical adsorption of hydrogen. This agrees with the data in [70] on the manifestation of TPD peaks A and B in single-wall nanotube samples saturated with hydrogen at an increased temperature (873 K), characteristic of chemisorption processes.

It is noted in [70], in particular, that many researchers concluded in favor of the possibility of a weak chemisorption mechanism (state) that is intermediate in relation to physical sorption and chemisorption. This open question was discussed in Section 2.

In connection with the above, we believe that it is useful to examine the TPD data on multiwall [62] and single-wall [63] nanotubes with the concentration of nanotubes and samples of the material larger than those used in [26]. The samples were saturated with hydrogen at room temperature and high pressures (up to 4 and 9 MPa, respectively). The thermal desorption activation energy for hydrogen E_a^{des} determined from Eqn (19) coincided (within the calculation error) with Q_I (Table 1).

The estimates made in Ref. [10] [via Eqn (25)] of the diffusion characteristic size for multiwall nanotube samples [52] with the mass of approximately 2 mg and with $D_{\rm I}$ corresponding to the TPD peak I (Table 1) yielded $L \sim 130-200 \,\mu\text{m}$, which is close to the value $L \sim 40-70 \,\mu\text{m}$ obtained above (see Table 2) for single-wall nanotube samples [26] with the mass about 1 mg.

The TPD data [63] on the β -dependence of $T_{\rm m}$ for clean single-wall nanotube samples (~90-95 mass%) with the mass about 1 g using Eqn (24) yield the value $K_0 \approx 0.2 \text{ s}^{-1}$, which clearly points to the diffusion nature of the process. Hence, using Eqn (22) and D_{01} from Table 1, we find that $L \sim 1$ mm, which, obviously, corresponds to the smallest linear size (thickness) of single-wall nanotube samples [63]. A similar value $L \sim 1$ mm is obtained [10] when Eqn (25) is used.

In [53], the samples were saturated with hydrogen at 295 K and a pressure of 1 to 9 MPa. An almost linear section of the Henry – Langmuir adsorption isotherm manifested itself. The adsorbate concentration at 9 MPa was nearly 0.3 mass% $(X = H_2/C \approx 1.8 \times 10^{-2})$, with the deviation of the isotherm X from the linear isotherm X^* given by $(X^* - X)/X^* \approx 0.14$, or about 14%.

To indirectly find (through experiments) the maximum sorption capacity of single-wall nanotube samples [63] corresponding to the Langmuir saturation $X_{\rm m} = ({\rm H}_2/{\rm C})_{\rm m}$, we can use the formula

$$X_{\rm m} = \left(\frac{\rm H_2}{\rm C}\right)_{\rm m} \approx \frac{XX^*}{X^* - X}\,,\tag{34}$$

which follows from Henry–Langmuir isotherm (14a), where $(X^* - X)/X^*$ is the relative deviation of the experimental sorption isotherm [63] from the linear pressure dependence, i.e., from the Henry isotherm, and X^* is the adsorbate concentration corresponding to the Henry isotherm (for a given experimental value of X corresponding to the Langmuir isotherm).

For single-wall nanotube samples [63], we thus obtain the maximum adsorbate concentration $X_{\rm m} \approx 0.13$, which agrees with the theoretical value of the total specific surface area of single-wall nanotubes [$S_{\rm tot}^{\rm th}$, Eqn (33)], i.e., with a certain average of the concentration over the entire (both external and internal) specific surface area of the adsorbate (the sorption monolayer model).

We note that when the adsorbate is located on a few sections of the sorption monolayer corresponding to the experimental value of the specific surface area S^{exp} , the

Parameter	Multiwall nanotubes [62]	Single-wall nanotubes		Single-wall nanohorns [31]
		[63]	[64], Fig. 11	
$E_{\mathrm{a}}^{\mathrm{des}},$ kJ $^{-1}(\mathrm{H}_2)$	20 ($\approx Q_I$, Table 1) Single-wall nanohorns (19), (24)	20 Equations (19), (24)	_	_
$egin{array}{c} K_0,\ { m s}^{-1} \end{array}$	~ 10 Equations (19), (24)	0.2 Equations (19), (24)	_	_
L, mm	0.13-0.2 Equations (22), (23), (25), Table 1	~ 1 Equations (22), (23), (25), Table 1	_	_
$\begin{array}{c} D(T_{\rm m}),\\ {\rm cm}^2{\rm s}^{-1} \end{array}$	$\sim D_{\rm I}(T_{\rm m})$ Equations (22), (23), (25), Table 1	$\sim D_{\rm I}(T_{\rm m})$ Equations (22), (23), (25), Table 1	_	—
$\Delta H^{ m ads} \ \Delta S^{ m ads}$		$ \sim \Delta H_{(13)I} \sim \Delta S_{(13)I} Equations (14), (15) for process I, Table 1 $	$ \sim \Delta H_{(13)\mathrm{I}} \sim \Delta S_{(13)\mathrm{I}} \mathrm{Equations} (14), (15) \mathrm{for process I, Table 1} $	$ \sim \Delta H_{(13)I} \sim \Delta S_{(13)I} Equations (14), (15) for process I, Table 1 $
$\begin{aligned} X &= \mathrm{H_2/C} \\ X_\mathrm{m} &= (\mathrm{H_2/C})_\mathrm{m} \\ X_\mathrm{m}^\mathrm{s} &= (\mathrm{H_2/C_{exp}^\mathrm{s}})_\mathrm{m} \end{aligned}$		$ \begin{array}{r} 1.8 \times 10^{-2} \\ 0.13 [\text{Eqn (34)}] \\ \end{array} $	$\leq 2 \times 10^{-2}$ ~ 5×10^{-2} [Eqn (34)] ≥ 0.20 [Eqn (35)]	≤ 0.15 ~ 0.2

Table 3. Sorption data for different carbon nanostructures.

maximum local concentration of the adsorbate can be estimated (in the order of magnitude) by the formula

$$X_{\rm m}^{\rm s} = \left(\frac{{\rm H}_2}{{\rm C}_{\rm exp}^{\rm s}}\right)_{\rm m} \approx \frac{XX^* S_{\rm tot}^{\rm th}}{S^{\rm exp}(X^* - X)}$$
(35)

that follows from (33) and (34).

The results in [63] for single-wall nanotubes are described fairly well by the adsorption isotherm for a type-I process [Eqn (14a)] with the following characteristics: $\Delta H^{ads} \approx -8.5 \text{ kJ mol}^{-1}(\text{H}_2)$, $\Delta S^{ads}/R \approx \Delta S_{(13)I}/R \approx -21$, and $X_{\rm m} = (\text{H}_2/\text{C})_{\rm m} \approx 0.13$ (rather than $X_{\rm m} \approx 0.5$, as assumed in examining the data in [26]).

The above arguments show that for single-wall [63] and multiwall [62] nanotube samples, a physical-like chemisorption process of type I occurs. The results of this analysis and of the comparison of TPD and sorption data for single-wall nanotubes, single-wall nanohorns, and multiwall nanotubes are listed in Table 3.

We arrive at a similar conclusion if we examine the experimental data in [64] on the sorption isotherms for samples of clean single-wall nanotubes and activated carbon. The samples were saturated with hydrogen at 273 - 323 K and pressures up to 10.7 MPa (Figs 11 and 12) and fabricated by a highly accurate volumetric method using a pressure-drop chamber.

For single-wall carbon nanotubes, the authors of [64] used the Clausius–Clapeyron equation to find the experimental value of the isosteric adsorption enthalpy $\Delta H^{ads} = -8.5\pm$ 1 kJ mol⁻¹(H₂) (the inset in Fig. 11), which is close to the value of $\Delta H_{(13)I}$ for chemisorption process I.

Using Eqn (34) to process the three adsorption isotherms (323, 298, and 273 K; see Fig. 11) for single-wall nanotube samples with the specific surface area $S^{\exp} \approx 609 \text{ m}^2 \text{ g}^{-1}$ yields the values $X_{\rm m} = (\text{H}_2/\text{C})_{\rm m} \approx 0.045 - 0.055$. Applying Eqn (35) gives the values $X_{\rm m}^{\rm s} = (\text{H}_2/\text{C}_{\exp})_{\rm m} \approx 0.19 - 0.24$, which are close, in the order of magnitude, to the carbohydride values listed in Table 1.

Estimates via expressions (14) and (15) for process I with the use of the experimental values of ΔH^{ads} and X/X_m yield $\Delta S^{ads}/R \approx -21.3 \approx \Delta S_{(13)I}/R$. The data in [64] presented in Fig. 12 suggest that only a fraction (about half) of the specific surface area S^{exp} of the single-wall nanotube samples in Fig. 11 is sorption-active; this points to the possibility of higher values, $X_m^s = (H_2/C_{exp}^s)_m \approx 0.4-0.5$. As noted in Ref. [64], the experimental values of the adsorbate concentration could be systematically underevaluated (by up to ~ 20%) because the effect of helium adsorption was ignored; this also points to the possibility of even higher values of X_m^s .

Similar processing, via Eqns (34) and (35), of the adsorption isotherm (298 K, up to 13 MPa, $X \approx 4.2 \times 10^{-2}$) for activated-carbon samples ($S^{exp} \approx 3135 \text{ m}^2 \text{ g}^{-1} \ge S_{\text{tot}}^{\text{th}}$) yields the value $X_{\text{m}} \approx X_{\text{m}}^{\text{s}} \approx 0.12$, which is close (in the order of magnitude) to the carbohydride value; $\Delta H^{\text{ads}} \approx -4 \text{ kJ mol}^{-1}(\text{H}_2)$.

Thus, we may assume that a physical-like chemisorption process of type I may occur in the single-wall nanotube samples used in [64]. We note that the researchers provide an extended definition of physical sorption without examining the nature and energies of the interaction while stressing



Figure 11. Hydrogen sorption isotherms [64] for single-wall nanotube samples (1.22 g) at 273 ($_{\odot}$), 298 ($_{\odot}$), and 323 K ($_{\Box}$). The inset shows isosteric heat (enthalpy) of adsorption of hydrogen by single-wall nanotube samples for different adsorbate concentrations.



Figure 12. Dependence of the sorption capacity of samples of the initial (\triangle) and ground (cut) (\blacktriangle) single-wall nanotube samples and activated carbon (\bigcirc) at 10.7 MPa and 298 K on their specific surface area, determined by the N₂-BET method [64].

the nondissociative nature and the relative fast kinetics of the sorption process. Obviously, a chemisorption process of type I formally satisfies such a definition.

The isotherms of hydrogen adsorption by clean samples of single-wall carbon nanotubes with conical (hornlike) ends (single-wall nanohorns, 95 mass%) that contained a relatively low amount (≤ 5 mass%) of metallic catalyst, amorphous carbon, and soot were studied in [31]. According to the data in Ref. [31], as the specific surface area of single-wall nanohorn samples increases by a factor greater than three (from $S_{\rm cl}^{\rm exp} \approx 308 \text{ m}^2 \text{ g}^{-1}$ to $S_{\rm ox}^{\rm exp} \approx 1006 \text{ m}^2 \text{ g}^{-1}$) due to the 'opening' of the nanotubes as a result of oxidation in oxygen at 693 K, the amount of the adsorbed hydrogen also grows by a factor of almost three (in saturation with hydrogen at high pressures $\sim 0.1 - 6.5$ MPa, and three temperatures, 303, 196, and 77 K). The adsorption isotherms [31] from the initial (closed) and oxidized (open) nanotubes (single-wall nanohorns) at the three temperatures are described fairly well by the Henry-Langmuir model for process I [Eqns (14) and (15) and Table 1]. The maximum adsorbate concentrations (saturation) were achieved with hydrogen saturation at 77 K and the pressure about 3 MPa for both the initial samples (~ 0.7 mass%, $\left(H_2/C\right)_{m,\,cl}\approx$ 0.04) and the oxidized samples $(2.5 \text{ mass}\%, (H_2/C)_{m, ox} \approx 0.15).$

Combining these data with the Henry–Langmuir model, we can obtain the averaged experimental values of the adsorption enthalpy $\Delta H_{\rm cl}^{\rm ads} \approx -4 \text{ kJ} \text{ mol}^{-1}(\text{H}_2)$ and $\Delta H_{\rm ox}^{\rm ads} \approx -6 \text{ kJ} \text{ mol}^{-1}(\text{H}_2)$, which are close to the experimental values of $\Delta H^{\rm ads}$ obtained in [78, 79] for single-wall nanotube samples, and also to the value of $\Delta H_{(13)I}$ in Table 1.

Using the Clausius-Clapeyron equation [68], close values for the isosteric enthalpy of hydrogen adsorption were obtained in [31]: ΔH_{cl}^{ads} in the range from -4.2 to -2.2 kJ mol⁻¹(H₂) and ΔH_{ox}^{ads} from -5.9 to -4.9 kJ mol⁻¹(H₂).

In examining the maximum values of the adsorbate content $(H_2/C)_{m,cl} \approx 0.04$ and $(H_2/C)_{m,ox} \approx 0.15$, we can assume (see Ref. [31]) that in the initial samples, the adsorbate is mainly localized on the sections of the external surface of the tubes (S_{cl}^{exp}) , which amounts to about 24% of the theoretical value $(S_{ext}^{th}, [29])$. In oxidized samples, approximately 70% of the adsorbate is localized on the sections of the internal surface of the tubes $(S_{ox}^{exp} - S_{cl}^{exp} \approx 7 \times 10^2 \text{ m}^2 \text{ g}^{-1})$, which amounts to approximately 54% of the theoretical value

of the internal surface of the tubes (S_{int}^{th} , [29]). Combining this with Eqn (33), we arrive at the maximum local concentrations of the adsorbate on the sorption sections of the external ($(H_2/C_{exp}^s)_m \sim 0.17$) and internal ($(H_2/C_{exp}^s)_m \sim 0.19$) surfaces of single-wall nanohorn samples [31] close to the carbohydride values (process I, Table 3).

It was suggested in [31] that physical adsorption of hydrogen is predominant in both the initial single-wall nanohorn samples and the oxidized samples. For oxidized samples, it was assumed that clusterization of hydrogen molecules occurs near the inner walls of the nanotubes and that a pseudohigh-pressure effect manifests itself near the nanoholes in the walls of the tubes (in intertubular cavities); all this increases the physical interaction between the internal surfaces of the tubes and hydrogen.

Murata et al. [31] also remarked on the fast kinetics of establishing equilibrium (taking about 10 minutes) when the single-wall nanohorn samples were saturated with hydrogen at 303, 196, and 77 K; the researchers noted the reproducibility (reversibility) of the adsorption – desorption isotherms, which in their opinion pointed to the physical nature of sorption.

However, such kinetics (supposedly diffusion kinetics) at 303 and 196 K may correspond to physical adsorption or to type-I chemisorption. Assuming that the smallest linear size (thickness) *L* of single-wall horn samples [31] varies from about 0.1 to 1 mm [31], we can use Eqns (22) and (25) to estimate the effective hydrogen diffusivity as $D \approx L^2/t \sim 2 \times$ $(10^{-7}-10^{-5})$ cm² s⁻¹. These values of *D* are comparable (at 303 and 196 K) to the values of *D*_I and the hydrogen surface diffusivity *D*^s, with the relatively low Van der Waals activation energy *Q*^s given in Table 1; at 77 K, special diffusion of hydrogen in the material may have occurred.

Unfortunately, Murata et al. [31] did not study the thermal desorption spectra of single-wall nanohorn samples and did not determine the activation energies of desorption or diffusion of hydrogen for different TPD peaks, which could have helped in identifying the nature of sorption processes in the material and in separating their contributions (see above and Section 4).

In this connection, it is logically reasonable to examine the data in [20] on the kinetics of hydrogen desorption at 293 K from electrochemically hydrogen-saturated composite samples (cylindrical pellets with the diameter about 7 mm and thickness $L \sim 0.1$ mm) fabricated by cold pressing of a mixture of single-wall nanotube bundles (10 mg) and gold powder (90 mg). The adsorbate content in single-wall nanotube samples [29] reached 0.9 mass% $(H_2/C \approx 5.4 \times 10^{-2})$. After ageing the samples at 293 K, about half of the adsorbate left the samples during the first hour and the relaxation time [see Eqns (21) and (22)] of this diffusion process α was $t_{\alpha} \approx 5$ min; it took 220 hours for the second half to leave the samples and the relaxation time of process β amounted to $\tau_{\beta} \approx 70$ h. Assuming that the characteristic diffusion path for both processes is equal to the thickness of the single-wall nanotube samples $(L \approx 0.1 \text{ mm})$, we can use Eqns (21) and (22) to obtain the value of diffusivity D_{α} for process α close to that of D_{I} at 293 K, i.e., corresponding to chemisorption process I, and the value $D_{\beta} = D_{I^*}$ for process β , which is smaller than D_I by three orders of magnitude but is larger than the diffusivity value $D_{\rm II}$ corresponding to chemisorption process II by a factor of 10^9 (Table 1). Hence, we may assume that for single-wall nanotube samples in [29], process α is comparable to chemisorption process I and process β is comparable to a chemisorption process of type I (or I^{*}) with somewhat higher values of the effective diffusion activation energy Q_{I^*} and of $\Delta H_{(13)I^*}$. In examining the data in [29] on the thermal adsorption for single-wall nanotube samples saturated with hydrogen at room temperature and the pressure 2 MPa, it may be assumed that the TPD peak at $T_m \approx 290$ K corresponds to process α , or I, and the TPD peak at $T_m \approx 800$ K corresponds to process β , or I^{*}.

The authors of [73] studied the isotherms of adsorption and desorption of hydrogen by single-wall carbon nanotubes, untreated with $S^{exp} \approx 420 \text{ m}^2 \text{ g}^{-1}$ and cleared of the metallic catalyst with $S^{*exp} \approx 1670 \text{ m}^2 \text{ g}^{-1}$, and by carbon nanofibers and activated high-purity carbon at ~ 290 K and pressures up to 2 MPa.

For clean single-wall nanotubes, the adsorption and desorption isotherms almost coincided (Fig. 13), i.e., as in [31], equilibrium had enough time to set in, obviously due to the fairly fast diffusion kinetics characteristic of the physical sorption or a type-I chemisorption process. Only the initial (close to linear) section of the Henry-Langmuir isotherm was evident, with the deviation from the linear behavior not exceeding 10%, while the adsorbate concentration at 2 MPa reached $(H_2/C)^* \approx 8 \times 10^{-3}$ (0.13 mass%). Hence, using Eqn (34), we obtain $(H_2/C)_m^* \approx 7.6 \times 10^{-2}$ [1.25 mass%, which corresponds to the averaged value of the maximum concentration of the adsorbate on the total (internal and external) surface of the nanotubes $(S_{tot}^{th}, [9, 29])$]. Assuming that the adsorbate is localized on the specific surface area of clean single-wall nanotubes, $S^{* exp}$, we use Eqn (35) to obtain the value $(H_2/C_{exp}^s)_m^* \approx 0.12$ for clean single-wall nanotubes. Taking the data in Fig. 14 into account, which imply that only $\sim 25\%$ of the surface of single-wall nanotubes cleared of the metallic catalyst is sorption-active, we obtain a revised value of the maximum local concentration $(H_2/C_{exp}^{s*})_m \sim 0.5$, corresponding to the carbohydride value for process I. We note that in a certain sense, the data in Fig. 14 [73] coincide with the data in Fig. 12 [64].

With this interpretation, the sorption-active sections of the surface of clean single-wall nanotubes [73] amount to only $\sim 16\%$ of the theoretical value S_{tot}^{th} of the total surface area of the tubes [9, 29]. A similar situation occurs with the clean single-wall nanotube samples in [31], where, as the above reasoning shows, the percentage of sorption-active sections of the surface does not exceed $\sim 12-39\%$ of S_{tot}^{th} .



Figure 13. Isotherms of sorption and desorption of hydrogen at room temperature by the initially untreated (*1* and *3*) and clean (*2* and *4*) single-wall nanotubes, respectively (from Ref. [73]).



Figure 14. Correlation between experimental values of the specific surface area of carbon materials (sorbents) and hydrogen sorption at room temperature and 2 MPa (from Ref. [73]).

The behavior of the initial untreated nanotubes described in [73] is in full agreement with the Henry-Langmuir adsorption isotherm (see Fig. 13) with the maximum saturation $(H_2/C)_m \approx 8.7 \times 10^{-3} (0.145 \text{ mass}\%)$ at approximately 1.4 MPa, which corresponds to the carbohydride value of the maximum local concentration $(H_2/C_{exp}^s)_m \approx 0.5$ [Eqn (33)]. The desorption isotherm for untreated single-wall nanotubes was characterized by a slight increase in the adsorbate content (from 0.145 to 0.152 mass%) as the pressure decreases from 2 to ~ 1 MPa, a plateau in the adsorbent content as the pressure decreases from ~ 1 to 0.5 MPa, and a slight decrease in the adsorbent content (down to 0.125 mass%) as the pressure lowers from ~ 0.5 MPa to zero. Obviously, in the untreated carbon nanotubes described in [73], the equilibrium in relation to the sorption process does not have enough time to set in, which points to a relatively slow (possibly diffusion) kinetics, characteristic of a certain type of hydrogen chemisorption. This may be caused by the presence of a metallic catalyst or other contaminants.

The isotherm of hydrogen adsorption by untreated singlewall nanotubes [73] at ~ 290 K and at pressures up to 2 MPa (see Fig. 13) coincides (as regards to the maximum saturation) with the isotherm of hydrogen adsorption by very 'dirty' single-wall nanotube samples [26] (Fig. 9b). This may be caused by the presence in the samples studied in [73, 26] (in contrast to the clean single-wall nanotube and nanohorn samples used in [73, 31]) of the content, distribution, and state of contaminants whose effect on hydrogen sorption has yet to be studied more thoroughly [28, 55, 73, 80].

For the single-wall nanotubes studied in [76], the values of the isosteric enthalpy of hydrogen adsorption at ~ 35 K (ΔH^{ads}) were found to be in the range from -7.5 to -2.5 kJ mol⁻¹(H₂) for the adsorbate concentrations H₂/C = (1.2-48) × 10⁻³. These values were compared with the experimental data for the enthalpy of hydrogen adsorption on the graphene surface of graphite [$\Delta H_{gr}^{ads} \approx$ -4.2 kJ mol⁻¹(H₂)] and the enthalpy of liquefaction (condensation) of gaseous hydrogen at 20 K [$\Delta H^{liq} \approx$ -0.9 kJ mol⁻¹(H₂)]. Similar values of the sorption characteristics were obtained in [81, 82].

The isotherms of hydrogen adsorption by multiwall nanotube samples ($S^{exp} \approx 137 \text{ m}^2 \text{ g}^{-1}$) and activated carbon AKh-21 ($S^{exp} \approx 3000 \text{ m}^2 \text{ g}^{-1}$) were studied in [75]. The initial sections of the Henry–Langmuir sorption isotherms became

evident at temperatures in the range 233–298 K and pressures ranging from ~ 0.1 to 11 MPa.

The value of the sorption capacity for AKh-21 at 233 and 6 MPa reached 0.9 mass%, with $H_2/C \approx H_2/C^s \approx 5.4 \times 10^{-2}$. The deviation of the isotherm from linear behavior was about 30%, which corresponded [in accordance with Eqn (34)] to $(H_2/C)_m \approx (H_2/C^s)_m \approx 017$.

For multiwall nanotube samples at 233 K and 10.3 MPa, the sorption capacity reached 0.27 mass% $[H_2/C \approx 1.6 \times 10^{-2}$ and $H_2/C_{exp}^s \approx 0.3$ (Eqn (33)]. The deviation of the isotherm from linear behavior amounted to about 16%, which corresponded to $(H_2/C)_m \approx 0.11$ [Eqn (34)] and the anomalous value of the maximum local adsorbate concentration $(H_2/C_{exp}^s)_m \approx 2$ [Eqn (35)], which is several times higher than the carbohydride value.

Based on the Clausius–Clapeyron equation [68], the values of the isosteric enthalpy of hydrogen adsorption for multiwall nanotube samples (ΔH^{ads}) were obtained in the range from -1.73 to -1.53 kJ mol⁻¹(H₂) for adsorbate concentrations ranging from 0.12 to 0.21 mass%, as well as for activated carbon AKh-21 [$\Delta H^{ads} \approx -6.4$ kJ mol⁻¹(H₂)] [75]. We note that the experimental value of ΔH^{ads} for multiwall nanotubes is relatively close to the enthalpy of liquefaction (condensation) of gaseous hydrogen at 20 K: $\Delta H^{liq} \approx -0.9$ kJ mol⁻¹(H₂) [76].

The sorption characteristics for activated carbon [75] can be interpreted using the monolayer chemisorption model (process I, Table 1). To interpret the sorption characteristics of multiwall nanotube samples [75], one can use the model of polylayer physical adsorption (adsorbate condensation) discussed below in Section 5.2.

5.2 Manifestation of polylayer physical adsorption initiated by monolayer chemisorption in single-wall nanotubes

We now discuss the data in [72] on the sorption of hydrogen by single-wall nanotubes (~ 10 mg, $S^{exp} \approx 5 \times 10^2 \text{ m}^2 \text{g}^{-1}$) and the initial graphite powder (~ 100 mg, $S^{exp} \approx 60 \text{ m}^2 \text{g}^{-1}$) saturated with hydrogen at fairly low pressures (from ~ 7 to 107 kPa, as in [26]) and two temperatures, 295 and 77 K (see Figs 15a and b). For the samples used in [72], in contrast to those studied in [26], the adsorption isotherm exhibited a specific (nonmonotonic) behavior at both temperatures, which can be interpreted as an oscillation about the linear concentration dependence corresponding to the Henry isotherm but without an explicit tendency toward the Langmuir saturation. For graphite samples [72] at both temperatures, there was a section in the isotherm close to the linear section of the Henry–Langmuir isotherm.

The adsorbate concentration in the single-wall nanotube samples studied in [72] at 295 K and 107 kPa reached ~ 0.93 mass% with H₂/C $\approx 5.6 \times 10^{-2}$ and H₂/C^s_{exp} \approx (H₂/C)Sth_{tot}/S^{exp} ≈ 0.29 [Eqn (33)]. In graphite samples, the concentration amounted to about 0.08 mass%, with H₂/C $\approx 4.8 \times 10^{-3}$ and H₂/C^s_{exp} ≈ 0.21 [72], i.e., within experimental error, and the adsorbate content was proportional to the adsorbate specific surface area S, which agrees with the sorption monolayer model. We note that the obtained values of the adsorbate local concentrations H₂/C^s_{exp} in single-wall and graphite samples [72] are close, in the order of magnitude, to the maximum (carbohydride) values (Table 1).

The adsorbate concentration in the single-wall nanotube samples studied in [72] at 77 K and 108 kPa reached ~ 2.37 mass%, with H₂/C \approx 0.15 and H₂/C^s_{exp} \approx 0.76 [Eqn (33)], while in the graphite samples investigated by the same researchers at 77 K and 103 kPa, the concentration amounted to about 0.17 mass%, with H₂/C \approx 1.0 × 10⁻² and H₂/C^s_{exp} \approx 0.44, Obviously, these values of the adsorbate local concentrations H₂/C^s_{exp} correspond to the maximum (carbohydride) values.

At the same time, according to preliminary estimates in [72], the isosteric (at $H_2/C \approx 5 \times 10^{-2}$) adsorption enthalpy for single-wall nanotube samples and for graphite samples amounted to only $\Delta H^{ads} \approx -1.2 \text{ kJ mol}^{-1}(H_2)$, which differs very much (by almost an order of magnitude) from the value of $\Delta H_{(13)I}$ of chemisorption process I.

The sorption capacity of single-wall nanotube and graphite samples used in [72] at 295 K and 107 kPa, calculated for $S \approx 1 \times 10^3$ m²g⁻¹, was given by approximately 1.9 and 1.3 mass%/(1000 m²g⁻¹), respectively. These values are relatively close to the similar characteristic value 1.5 ± 0.2 mass%/(1000 m²g⁻¹) obtained in [29] for electrochemically hydrogen-saturated single-wall nanotube and graphite samples with the specific surface area ranging



Figure 15. Isotherms of hydrogen sorption at 295 K (a) and 77 K (b) by single-wall nanotube samples (●) and initial graphite (▲) (from Ref. [72]).

from 50 to $1200 \text{ m}^2 \text{ g}^{-1}$ (experimental values), which points to the surface nature (localization) of the sorption processes considered.

The authors of [72] noted that for single-wall and graphite samples at 77 K, the indirect values (that follow from their sorption data) of the local surface concentrations of the adsorbate cannot be explained by the known mechanisms of physical monolayer sorption because they substantially exceed the maximum adsorbate concentrations corresponding to the adsorbate monolayer structure commensurate with the graphene structure ($H_2/C^s \approx 0.17$) and with the closepacked adsorbate monolayer structure, not related to the graphene structure ($H_2/C^s \approx 0.25$).

It is quite significant that the hydrogen adsorption isotherms of the single-wall nanotube samples studied in [72] do not reach a saturation plateau (see Fig. 15), i.e., there is no tendency toward Langmuir saturation even at 77 K (in contrast to the case with the single-wall nanotube samples in [26]). Another important property is that the maximum (carbohydride) values of the adsorbate concentration manifest themselves only when local concentrations are considered, i.e., when recalculating the experimental values of H_2/C using equation (33) for local values of H_2/C_{exp}^s . This approach is used under the assumption that the entire adsorbate is localized on the experimentally determined specific surface area S^{exp} of single-wall nanotubes. The physical interpretation of such a situation may be that the external surfaces of single-wall nanotube bundles, or the interbundle (interface) surfaces, play a dominant role in sorption (for kinetic and/or other reasons), compared with the role of nanotube surfaces inside the bundles. In this model, the experimental value of the specific surface area of single-wall nanotube samples agrees with the theoretical value of the specific interbundle surfaces, which is given by

$$S_{\rm b}^{\rm th} \approx S_{\rm ext}^{\rm th} \frac{d_{\rm NT}}{d_{\rm b}} \,,$$
 (36)

where $d_{\rm NT}$ and $d_{\rm b}$ are the respective diameters of individual nanotubes and bundles of single-wall nanotubes (see Figs 1 and 2) and $S_{\rm ext}^{\rm th} \approx 1.3 \times 10^3 \, {\rm m}^2 \, {\rm g}^{-1}$ is the theoretical value of the external surface area of individual nanotubes (taken from Ref. [29]). Substituting the experimental values $d_{\rm NT} \approx 1.3 \, {\rm nm}$ and $S_{\rm b}^{\rm th} \approx S^{\rm exp}$ (taken from Ref. [72]) in Eqn (36), we obtain the typical value of the diameter of single-wall nanotube bundles $d_{\rm b} \approx 3.4 \, {\rm nm}$.

The study of the sorption data in [72] shows that a specific type of physical adsorption may occur: there may be polylayer intercalation (or condensation) of the adsorbate in interbundle regions of single-wall nanotubes, in which the interbundle (interface) surfaces are, apparently, decorated with a monolayer of the adsorbate, close to the carbohydride adsorbate monolayer in both composition and structure. In other words, such a specific physical adsorption in the interbundle nanoregions of single-wall nanotubes may be initiated mainly by the formation of a carbohydride adsorbate monolayer on the interbundle (interface) surfaces, which in turn may be due to a certain chemisorption process (of type I and/or II, Table 1).

The validity of this interpretation of the data in [72] is confirmed, in particular, by the proximity of the experimental value of the isosteric adsorption entropy $\Delta H^{ads} \approx -1.2 \text{ kJ}$ mol⁻¹(H₂) at H₂/C $\approx 5 \times 10^{-2}$ to the experimental values of the liquefaction enthalpy of gaseous hydrogen, ΔH^{liq} , examined in Refs [29, 31, 76], and to the results of the analysis and comparison of the sorption data obtained in [72, 74, 77], which we examine below.

Of special interest are the results in [77] (Fig. 16), where hydrogen sorption by single-wall nanotube samples $(S^{exp} \approx 285 \pm 5 \text{ m}^2 \text{g}^{-1})$ and activated carbon (Saran) $(S^{exp} \approx 1600 \text{ m}^2 \text{g}^{-1})$ were studied at 80 K and pressures up to 12 MPa. The 1996 Nobel Prize winner in chemistry R E Smalley collaborated in this research, but its results have never been reproduced by other researchers.

For the samples of activated carbon (Saran), a Henry– Langmuir sorption isotherm appeared under pressures up to approximately 7 MPa (curve 4 in Fig. 16), with the maximum saturation at pressures ≥ 7 MPa, $(H_2/C)_m \approx 0.2$, or at the maximum local adsorbate concentration $(H_2/C_{exp}^s)_m \approx 0.3$ [Eqn (33)] corresponding to the sorption (close to the carbohydride) monolayer model. The adsorption enthalpy for the Saran samples amounted to $\Delta H^{ads} \approx -3.7$ kJ mol⁻¹(H₂) (the indirect experimental value in [77] obtained using the tabulated data on the chemical potential of gaseous H₂).

For single-wall nanotube samples, a Henry–Langmuir sorption isotherm manifested itself to a certain extent under pressures up to approximately 2 MPa (curves 3 in Fig. 16). The adsorbate concentration at 2 MPa reached the value $H_2/C \approx 4 \times 10^{-2}$, which agrees with the local concentration $H_2/C_{exp}^s \approx 0.37$ [Eqn (33)] close to the carbohydride value (~ 0.5, Table 1).

We note that the value of S^{exp} for the single-wall nanotube samples studied in [77] is close to the theoretical value S_b^{th} of the specific surface area of the interbundle (interface) surface [Eqn (36)]. The diameter of the bundles in the samples considered ($d_b \approx 6-12$ nm) is approximately ten times greater than the diameter of individual nanotubes ($d_{NT} \approx 1.2$ nm). Hence, we may assume that at ≥ 2 MPa, the adsorbate concentration in the sorption monolayer on the

1.0

0.8

0.6

0.4

0.2

0

2

4

Atomic ratio H/C



6

Hydrogen pressure, MPa

8

10

12

interbundle (interface) surface [77] agrees with the carbohydride value (in the order of magnitude).

When the initial single-wall nanotube samples were saturated with hydrogen at higher pressures (from ~ 2 to ~ 7 MPa; curve *1* in Fig. 16), an anomalous increase (with respect to the Henry–Langmuir isotherm) in the adsorbate concentration was registered, which reached $H_2/C \approx 0.52$ (8.0 mass%) at 7 MPa. This agrees with the local concentration $H_2/C_{exp}^s \approx 4.7$ [Eqn (33)] and is ten times higher than the carbohydride value. In the next rounds of hydrogen saturation of single-wall nanotube samples, as the pressure increased from ~ 2 to ~ 12 MPa (curves *3* in Fig. 16), an anomalous increase in the adsorbate concentration up to $H_2/C \approx 0.47$ (7.3 mass%) was also registered, corresponding to the anomalous value $H_2/C_{exp}^s \approx 4.3$.

The authors of [77] assumed that in their single-wall nanotube samples at $\sim 2-4$ MPa, the interbundle (interface) surfaces of the nanotube bundles [Eqn (36) and Fig. 2] were filled primarily with the adsorbate (within a monolayer). They also assumed that at higher pressures (4-12 MPa), the adsorbate (the sorption monolayer) structure undergoes a first-order phase transition, which makes the bundles 'fall apart' such that only individual nanotubes are present, with the physical (monolayer) adsorption of hydrogen occurring on their surfaces ($S_{\text{ext}}^{\text{th}}$ or $S_{\text{tot}}^{\text{th}}$, [29]). Using this model, the indirect experimental value of the cohesion energy for single-wall nanotubes in the bundles was found as $\sim 0.5 \text{ kJ mol}^{-1}(\text{C})$. It was then assumed that the 'falling apart' of bundles (with the nanotubes becoming independent of each other) is initiated by the high pressure of gaseous H₂ (> 4 MPa) in the course of the phase transition in the adsorbate structure at 80 K. The authors of [77] noted that their experimental value of hydrogen sorption for single-wall nanotubes (H₂/C \approx 0.47 at 11.7 MPa) corresponds to the maximum possible value of the adsorbate concentration for any adsorbate based on carbon (obviously, within the sorption monolayer model). The absence of the maximum (Langmuir) saturation on the sorption isotherms for their single-wall nanotube samples was explained by the special features of the kinetics of successive bundle disintegration.

The isotherm of hydrogen adsorption by clean single-wall nanotubes ($S^{exp} \approx 800 \text{ m}^2 \text{ g}^{-1}$) and by samples of activated carbon ($S^{exp} \approx 2800 \text{ m}^2 \text{ g}^{-1}$) was studied in [74] at 294 K and pressures up to 30 MPa (Fig. 17). Figure 17 shows that when single-wall nanotube samples were saturated with hydrogen, the Langmuir saturation $(\text{H}_2/\text{C})_{\text{m}} \approx 0.055$ revealed itself fully at pressures ≥ 30 MPa, which corresponds to $(\text{H}_2/\text{C}_{\text{exp}})_{\text{m}} \approx 0.18$ [Eqn (33)] and agrees with the sorption monolayer model. No disintegration of the bundles was recorded in this case, although the pressures were ten times higher than those used in [77], which, in particular, corroborates the data on the electric resistivity of the samples due to hydrogen sorption at different pressures [74].

It therefore follows that high pressure does not play a role in the anomalous sorption of hydrogen (see Fig. 16), nor is it the main reason for the occurrence of the anomalous sorption or disintegration of bundles of single-wall nanotubes, contrary to the assumption in [77].

We note that the experimental value of the maximum sorption capacity (0.9 mass%, or $H_2/C)_m \approx 0.055$) of the single-wall nanotube samples used in [74] (see Fig. 17) agrees with the reduced sorption capacity value ~ 1.1 mass%/(1000 m² g⁻¹), which is quite close to the similar characteristic, $1.5\pm0.2 \text{ mass}\%/(1000 \text{ m}^2 \text{ g}^{-1})$, for carbon sorbents



Figure 17. Hydrogen sorption isotherms at 294 K for clean single-wall nanotubes (*1*) and by activated carbon (*2*) (from Ref. [74]).

obtained in [29]. The sorption data gathered in [74] for single-wall nanotube samples can be described via the Henry–Langmuir adsorption isotherm using Eqns (14) and (15) with the values of ΔH^{ads} and ΔS^{ads} close to those for chemisorption process I ($\Delta H_{(13)I}$ and $\Delta S_{(13)I}$), listed in Table 1.

The Henry–Langmuir adsorption isotherm with the maximum saturation (at pressures ≥ 35 MPa) of the order of 1.5 mass% $[(H_2/C)_m \approx 0.09]$ was recorded (but was less pronounced) in [74] for samples of activated carbon (see Fig. 17). This corresponds to a relatively low reduced value of the sorption capacity, ~ 0.5 mass%/(1000 m² g⁻¹). We can therefore assume that only the sorption-active sections of the specific surface area become saturated and, apparently, the percentage of these sections is not higher than 50% of the experimental value.

The saturated local surface concentration in single-wall nanotube samples used in [74] at 30 MPa $[(H_2/C_{exp}^s)_m \approx 0.18]$ is much lower than the carbohydride value (~ 0.5). This differs from the situation with single-wall nanotube samples in [77], for which the local adsorbate concentration on the interbundle surfaces reached the carbohydride value $H_2/C_{exp}^s \approx 0.5$ at 2–4 MPa and 80 K. As the pressure grew to 12 MPa, an anomalous (unsaturated) increase in hydrogen sorption was recorded in single-wall nanotube samples [74] to the values of the local adsorbate concentration H_2/C_{exp}^s , which were found to be ten times higher than the carbohydride value (see Fig. 16).

We note in this connection that the adsorbate concentration in single-wall nanotube samples in [72] at 77 K and 108 kPa reached the value $H_2/C \approx 0.15$ (Fig. 15b), corresponding to the local concentration $H_2/C_{exp}^s \approx 0.76$ [Eqn (33)], which is much higher than the carbohydride value. This is obviously closer to the situation with the single-wall samples in [77] than to that with the samples studied in [74].

It can be assumed (accepting the concept in [77]) that the process of anomalous adsorption of hydrogen by the samples studied in [77] at 80 K and pressures $\sim 2-12$ MPa is related to the 'intergrowth' of a two-dimensional carbohydride phase from the interbundle surfaces along the surface grooves depicted in Fig. 2 into the inner regions of the nanotube bundles, i.e., on the surface of the constituent nanotubes; this

leads to disintegration of the bundles into separate nanotubes with a carbohydride monolayer coating.

Another model (suggested by the results of the analysis of the data in [72] and Fig. 15) of such anomalous sorption, shown in Fig. 16, may be related to the physical polylayer adsorption (polylayer intercalation, clusterization [31], and/ or condensation [29, 30] of the adsorbate) in the boundary nanoregions between the nanotube bundles, occurring when carbohydride concentrations on the bundle surfaces are reached (the chemisorption stage). To a certain extent, such a two-stage sorption model resembles the model of monolayer adsorption and the subsequent condensation of the adsorbate (at subcritical temperatures) proposed in [30]. As noted in Refs [29, 30], the question about the adsorbate condensation at ~ 80 K (in the cases studied in [72] and [77]), which is much higher than the critical temperature (33 K), remains open; the problem has been studied theoretically in [83] using the molecular dynamics method. There is also the question about the small experimental values S^{exp} of the specific surface area of single-wall nanotube samples (in particular, in Ref. [77]) compared with the theoretical value S_{tot}th; according to the data in [29, 30, 84], the sorption is directly proportional to S^{exp} in such cases. This situation may correspond to the monolayer model for both physical sorption [69] and type-I chemisorption (Table 1).

The analysis and comparison of the data in [72, 74, 77] show that the anomalous sorption of hydrogen by single-wall nanotube structures (Figs 15b and 16) can in any case be explained only by a model that accounts for both the monolayer (undoubtedly, chemisorption) stage of the process and the polylayer stage initiated by the monolayer stage. Obviously, the polylayer stage constitutes a special physical adsorption process of the adsorbate condensation type that runs at subcritical temperatures. This process probably occurs due to the absence in single-wall nanotube structures (in contrast to activated carbon) of a rigid 'frame' that prevents the nanotube bundle structure from disintegrating and/or 'swelling' caused by polylayer intercalation and/or condensation of the adsorbate.

Special polylayer physical adsorption, in addition to chemisorption, could possibly have occurred in single-wall nanotube samples (50–70 mass%, $S_i^{exp} \approx 270 \text{ m}^2 \text{ g}^{-1}$, and $S_c^{exp} \approx 180-470 \text{ m}^2 \text{ g}^{-1}$) with a considerable amount of soot and metallic catalyst, untreated (S_i^{exp}) or the chemically cleaned (S_c^{exp}) with oxygen and/or acids (HCl or HNO₃) and saturated with hydrogen at 87–77 K under pressures amounting to 0.001–1.6 MPa.

The sorption capacity of the most defective (treated with HNO₃) single-wall nanotube samples studied in [87] $(S_c^{exp} \approx 250 \text{ m}^2 \text{ g}^{-1})$, which were saturated with hydrogen at 77 K, reached the maximum hydrogen saturation ~ 6.4 mass% $[(H_2/C)_m \approx 0.42]$ at pressures ≥ 0.2 MPa. This agrees with the anomalous local concentration $(H_2/C_{exp}^s)_m \approx 4.4$ [Eqn (33)], which is ten times higher than the carbohydride value. When the samples were saturated with hydrogen at 87 K, the maximum saturation (~ 5.0 mass%) was reached at pressures ≥ 0.6 MPa. The obtained anomalous (for monolayer adsorption) values of $(H_2/C_{exp}^s)_m$ suggest that polylayer adsorption is possible.

For the remaining samples, either the initial or the treated, the sorption capacity at 77 K and at pressures up to 1.6 MPa did not exceed 1.0-3.3 mass%, i.e., there was no significant correlation between the adsorbed hydrogen content and the size of the specific surface (S_i^{exp} and S_c^{exp}) determined from the BET isotherms for N_2 at 77 K. This may correspond to polylayer adsorption.

The isosteric hydrogen adsorption enthalpy determined in [87] for the most defective single-wall nanotube samples with nanoholes in tube walls ($S_c^{exp} \approx 250 \text{ m}^2 \text{ g}^{-1}$) amounted to $\Delta H^{ads} = -12 \pm 2 \text{ kJ mol}^{-1}$ (without specifying the corresponding adsorbate concentration). For instance, from the sorption data gathered in [87], at a concentration of about 4 mass%, we find that $\Delta H^{ads} \approx -8 \text{ kJ mol}^{-1}$. The values of ΔH^{ads} are ten times higher in the absolute value than the hydrogen liquefaction enthalpy ΔH^{liq} [76] and are close to the energy characteristics of the sorption process [26, 70] discussed in Section 5.1, a process corresponding to TPD peak A (Figs 9a and 10 and Table 2).

The authors of [42, 85–87] noted the high experimental value of the adsorption enthalpy but assumed, based on the analysis of their data gathered by various methods (Raman spectroscopy, thermal gravimetry, and measurements of the thermal electromotive force and electric resistivity), that physical adsorption is predominant.

At the same time, the authors of [42] did not exclude the possibility of interpreting their data on the thermal electromotive force and electric resistivity of hydrogen-saturated single-wall nanotube samples on the basis of the physical adsorption mechanisms and on the basis of chemisorption with an interaction weaker than that in the common covalent C-H bonds.

The kinetics of hydrogen saturation of single-wall nanotube samples in the form of 'mats' with thickness $L \approx 1$ mm at 500 K and 0.1 MPa and the kinetics of isothermal desorption of hydrogen from samples in a vacuum at 500 K were studied in [85]. Both processes ran as first-order reactions with the relaxation time $\tau \approx 1$ h. Assuming (see Ref. 10) that the limiting stage is the diffusion of hydrogen molecules from the surface or in the direction of the sample surface, we obtain the diffusivity $D_{\rm I} \approx L^2/\tau$ corresponding to chemisorption process I. In this case, therefore, we can speak of a diffusion manifestation of the mechanism of physical-like chemisorption.

It was noted in [42, 85–87] that the sorption capacity of approximately 7.3 mass% (without saturation) was achieved for single-wall nanotube samples studied in [77] at 77 K and the pressure ~ 12 MPa (see Fig. 16), i.e., at much higher pressures than those used in [87]. We note that the value of the maximum sorption capacity of single-wall nanotube samples obtained in [87] (~ 6.4 mass% (saturation) at 77 K and ~ 0.2 MPa) is comparable with the data in [72]: ~ 2.4 mass% (without saturation) at 77 K and ~ 0.1 MPa (Fig. 15b). The values of the sorption capacity and ΔH^{ads} obtained by [87] and also the nature (saturability) of the adsorption isotherm and the pressure range are comparable with the characteristics of the sorption process studied in [26] (and examined in Section 5.1) corresponding to TPD peak A (Fig. 9a and Table 1).

Obviously, the Raman spectra studied in [42, 85–87] for a number of carbon materials interacting with hydrogen at 85 K and 0.4 or 0.8 MPa contain information about sorption carbon centers on the graphene surface for highly oriented pyrolytic graphite, fullerite C₆₀, and single-wall carbon nanotubes. It is useful to consider this information when examining the nature of the interaction of these materials with hydrogen. However, some doubts can be expressed regarding the assumption made these researchers that one of the *Q*-components of the spectrum, 4161.3 cm⁻¹ and 4155.4 cm⁻¹, which manifests itself for all these materials (the only component of the spectrum of pyrolytic graphite and the main component for the spectrum of single-wall carbon nanotubes at 0.8 MPa) is caused by the hypothetical surface gaseous phase of H₂. Based on the results in the previous sections, we can assume that physical-like chemisorption (type-I process, Table 1) contributes to this situation.

Raman spectroscopy was used in [88] to study the mechanism of hydrogen adsorption by carbon materials at the hydrogen saturation pressures 0.2-6.5 MPa and the temperature 20-3000 K. The researchers assumed in [42, 85-87] that the physical adsorption dominates, because they observed small shifts of peaks corresponding to a very small charge transfer during the hydrogen sorption. However, they did not consider the possibility of physical-like chemisorption, for which, as can be expected, charge transfer is negligible.

Raman and IR spectroscopies were used in [89] to study the configurational state of hydrogen in nanostructured (as a result of mechanical synthesis) graphite. An oscillation signal (peak) corresponding to the covalent C-H bond was observed in the IR spectrum (mostly for the $C-H_2$ configuration, which is obviously comparable with model H in Fig. 8 for chemisorption process II). No such C-H peak was observed in the Raman spectrum.

Regarding the results in [89], we must note that two to three TPD peaks (see Fig. 7) were observed in nanostructured graphite in [14, 53-56], which, according to the analysis in Refs [10, 17] (Section 3, Table 1), correspond to chemisorption processes II, III, and/or IV. This suggests that such processes do not manifest themselves fully in Raman spectra and that only one of them (apparently, process II) manifests itself in IR spectra (in contrast to processes III and IV). This agrees with the experimental data examined in Section 5.3 below.

In this connection, we also mention the data in [90] on X-ray adsorption spectra (NEXAFS) for nanostructured carbon films saturated with hydrogen under the pressure 0.12 MPa at room temperature. These results indicate that chemisorption dominates in the given conditions (cf. theoretical results in [91, 92], which suggest that physical adsorption of hydrogen at room temperature plays a negligible role in carbon nanotubes or in highly defective graphite). At the same time, according to the theoretical data in [35, 93], physical sorption of hydrogen may dominate under certain conditions.

5.3 Physical adsorption and chemisorption in single-wall nanotubes and GNFs saturated with hydrogen at 9 GPa

In [94], single-wall nanotube samples (50-60%) and GNF (~90%) were saturated with hydrogen under the pressure 9 GPa at 623 K (18 hours, first stage), then at 723 K (6 hours, second stage), followed by cooling to 133 K (third stage), lowering the pressure to atmospheric, and storing the samples in liquid nitrogen. The total hydrogen content obtained by burning the samples in a current of oxygen reached 6.8 mass% (H/C \approx 0.88) for single-wall nanotubes and 6.3 mass% (H/C \approx 0.81) for GNF.

In [95], single-wall nanotube samples (80-85%) were saturated with hydrogen under the pressure 5 GPa at 623 K (21 hours, first stage), then at 733-763 K (9 hours, second stage), followed by cooling to room temperature (third stage) and lowering the pressure to atmospheric. The total hydrogen

content obtained by burning the samples in a current of oxygen reached 10.8 ± 0.1 mass% or, calculated for hydrogen, 5.4 mass% (H/C ≈ 0.68).

The total content of hydrogen in single-wall nanotube samples studied by these two groups of researchers [94, 95] is proportional, in a satisfactory approximation, to the square root of the hydrogen pressure, which corresponds to the Sieverts dissociative – absorption isotherm [Eqn (5a)].

We believe that it is useful to study in detail, systematize, and interpret the fundamental results obtained in [94, 95] using the X-ray diffraction method and IR spectroscopy. The measurements [94] of the pressure of the gas released during vacuum heating of hydrogen-saturated single-wall nanotube samples and GNF (from 77 to 873-923 K, with the rate 20 K min^{-1}) have shown that three desorption processes were running: (α) at ~ 175-280 K, with ~ 0.45 and 0.15 mass% of hydrogen released, respectively; ($\beta + \gamma$) at ~ 773-873 K, with ~ 5.3 and 4.8 mass% of hydrogen released, without taking the possible release of a small amount (~ 0.05) of hydrocarbons into account [94, 95]; and (γ) at ≥ 823 K, the remainder, ~ 1 mass%.

The X-ray diffraction patterns of hydrogen-saturated GNF samples studied in [94] (Fig. 18) contained a broad intense peak near 19° instead of a very strong, narrow reflection of the (002) line of graphite at $2\theta = 26.5^{\circ}$, characteristic of the initial samples. This corresponds to an increase in the interplanar spacing between the graphene layers in all graphite nanofibers by approximately 40%, from 3.36 Å in the initial GNF to 4.67 Å in the hydrogen-saturated GNF. It is also an indication that substantial microstrain is generated in these layers. The next graphite reflections are noticeably shifted toward small angles, and only the catalyst line remains in place.

A decrease in the total adsorbate content by ~ 43% (6.3 mass% of hydrogen) in hydrogen-saturated GNF samples subjected to vacuum annealing at about 773 K in the course of 1 to 10 hours, i.e., the removal of about 2.7 mass% of hydrogen during the annealing process, led to the emergence (see Fig. 18) of two very strong reflections (at $2\theta \approx 19.9^{\circ}$ and 24.0°), which are shifted toward each other, are close in intensity, and are extremely broadened. The authors of [94] believe that this constitutes the diffraction pattern of a two-phase state. Obviously, this indicates that about 50% of nanofibers with an interplanar spacing for the graphene layers somewhat smaller than 4.67 Å and about 50% of nanofibers with an interplanar spacing larger than 3.36 Å, with a high level of microstrain in both cases, are present in such samples.

After two cycles of heating the hydrogen-saturated GNF samples [94] to 873 K, which reduced the total adsorbate content by $\sim 81\%$ (i.e., $\sim 5.1\%$ of hydrogen was removed), the peak at $2\theta \sim 19^\circ$ in Fig. 18 either virtually disappeared or manifested itself as an extremely broadened peak of low intensity; instead, a high peak appeared at $2\theta \sim 26^{\circ}$ (the reflection of the (002) graphite line) shifted toward small angles. This agrees with the incomplete removal of adsorbed hydrogen (the remainder amounts to ~ 1.2 mass%) and suggests that the predominant fraction of nanofibers in such samples has interplanar spacings that are close to the normal value (3.36 Å) and a low level of microstrain in the graphene layers. For the other nanofibers, the situation is quite different. Prolonged (6-hour) vacuum annealing of the hydrogen-saturated GNF samples at 973 K fully restored the initial pattern: it led to a strong, narrow (002) reflection at $2\theta = 26.5^{\circ}$, which corresponds to the normal interplanar spacing between the graphene planes and to the absence of microstrain in GNF.

The diffraction patterns of hydrogen-saturated singlewall nanotube samples studied in [94], in contrast to those of the initial single-wall nanotube samples, exhibited a broad peak with a predominant intensity near 18.4° , while the narrow reflection of the (002) graphite line near 26.5° becomes very pronounced. This may be because such samples contain up to 40-50 mass% of graphitized (under thermobaric treatment) multilayer nanoparticles, most of which, obviously, have an increased (by roughly 40%) interplanar spacing and an increased level of microstrain in the graphene layers. The other graphite nanoparticles have an interplanar spacing close to normal (3.36 Å), with no essential microstrain in the graphene layers.

The decrease in the total adsorbate content in the hydrogen-saturated single-wall nanotube and GNF samples [94] subjected to vacuum annealing at about 773 K for 1 to 10 hours amounted to ~ 37% and ~ 43%, respectively (~ 2.5 and ~ 2.7 mass% of hydrogen) and was found to lead to the complete disappearance of narrow absorption lines in the IR spectra at 2860 and 2920 cm⁻¹, a characteristic feature of the valence vibrations of the C–H bond, and also to the disappearance of the broad adsorption line at ~ 1200 cm⁻¹ (curves 2 and 3 in Fig. 19).

This implies that $\leq 37\%$ (for single-wall nanotube samples) and $\leq 43\%$ (for GNF samples) of the total content of the adsorbed hydrogen is characterized by IR adsorption lines typical of the valence vibrations of the C-H bond and, obviously, correspond to process β . It can also be assumed that $\geq 60\%$ of the total content of the adsorbed hydrogen corresponds to process γ , characterized by the absence in the IR spectra of vibrational modes inherent in the C–H bond, and causes (in the majority of cases) a sharp increase (up to 40%) in the interplanar spacing between the graphene layers (for GNF samples). The structural reflections in the diffraction patterns of single-wall nanotube samples are obviously caused by the presence in these samples of carbon multilayer nanoparticles (up to 40-50 mass%), which crystallize (graphitize) under thermobaric treatment and participate in the sorption and adsorption of hydrogen.

In [94], process α was related to the physical adsorption of hydrogen molecules on graphene layers; for this, the authors refer (without a sufficient analysis) to the results in [85], which were discussed in Section 5.2. They also relate process β to the formation of covalent C-H bonds, i.e., to chemisorption. Process γ , inactive in the IR spectrum but responsible for the anomalous change of the diffraction pattern of the multilayer structure of GNF subjected to hydrogen saturation (see Figs 18 and 19), is related to molecular hydrogen located (intercalated) between the graphene layers in the bulk of the nanofiber. The concept of a buildup of molecular hydrogen between graphene layers is recalled here; this concept was formulated in [14, 96] in studying the mechanical synthesis of hydrogen with graphite (upon grinding in ball mills) and in [52], where the interaction of atomic hydrogen and graphite was studied. The results of the critical, constructive analysis, processing, and interpretation of the data in [14, 52, 96], presented in Refs [10, 97], is not taken into account in [94]. The authors believe that they were able to fabricate thermally stable compounds containing up to 6.8 mass% of hydrogen, whose larger fraction is in a new state characterized by the absence of vibrational C-H modes in the IR spectra.



Figure 18. X-ray diffraction patterns of GNF and single-wall nanotube samples at room temperature in the initial state after hydrogen saturation at 9 GPa (6.8 and 6.1 mass% H_2), after removal of about 40% of the adsorbate (4.3 and 3.6 mass% H_2), after degassing annealing to 873–923 K (1.7 and 1.2 mass% H_2), and after prolonged annealing at 973 K (GNF). The MPG-6 graphite diffraction pattern is presented for comparison. The dashed diagrams for Fe and Cu indicate the presence of a catalyst impurity in GNF (from Ref. [94]).

We therefore believe that there must exist a better interpretation of this state corresponding to process γ , and a more detailed description of process β based on the following experimental facts:

(1) the appearance of a Sieverts dissociation – sorption isotherm for single-wall nanotube samples studied in [94, 95], which points to the atomic rather than molecular state of the larger fraction the adsorbate (γ);

(2) the desorption temperatures for process γ being higher than those for process β , which points to a higher desorption activation energy ($Q_{\gamma} > Q_{\beta}$);

(3) the absence of vibrational C–H modes in the IR spectra (at $500-5000 \text{ cm}^{-1}$, Fig. 19) for process γ (in contrast to process β), which obviously points to a significant difference in the mechanisms of these processes;

(4) the anomalous change in the diffraction pattern (see Fig. 18) of the multilayer structure of GNF for process γ , caused by an increase (up to 40%) in the interplanar spacing between the graphene layers in the GNF, which indicates that the adsorbed hydrogen is localized (γ) between the graphene layers;

(5) the presence in the single-wall nanotube samples studied in [94] of up to 40% of graphite multilayer



Figure 19. IR diffuse reflection spectra of GNF and single-wall nanotube samples [94] in the initial state, after saturation with hydrogen at 9 GPa, after removal of about 40% of the adsorbate (hydrogen), and after degassing annealing. Room temperature.

nanoparticles and the presence of up to 20% of such nanoparticles in the single-wall nanotube samples studied in [95], together with the strong agglomeration of nanotubes noted in Ref. [95] (in the form of strands, microcrystalline films, and 'rugs' with a polycrystalline structure), i.e., the presence in the single-wall nanotube samples used in [94, 95] of graphite multilayer nanostructures typical of the GNF samples used in [94], in which the sorption process γ may run;

(6) the appearance (studied in [95]) in the mass spectra of the gases released in the course of a multistage prolonged (many-hour) heating up to 673 K in a vacuum of deuterated single-wall nanotube samples, the prevailing contribution of hydrocarbons, and, at higher temperatures of the multistage heating process (773 K for 3 hours and 823 K for three hours), the appearance of the prevailing contribution of deuterium and HD molecules; and

(7) (a) the manifestation of only one C-H peak in the IR spectrum of nanostructured graphite studied in [89] (see Section 5.2), which basically corresponds to the C-H₂ configuration comparable to model H in Fig. 8 for chemisorption process II; (b) manifestation in such a material of two to three high-temperature TPD peaks [14, 53-56, 96] (chemisorption processes II, III, and/or IV, Table 1 and Fig. 7), two peaks in the NMR spectrum (of the Gaussian and Lorentzian types) [14, 65], and two peaks corresponding to C-B bonds, 0.11 and 0.18 nm long, in the spectrum of the neutron-diffraction radial distribution [14]; (c) the manifestation of two high-temperature TPD peaks corresponding to chemisorption processes II and III in hydrogen-saturated GNF samples [12] (see Fig. 6); (d) the manifestation of a high-temperature TPD peak corresponding to chemisorption

process II in hydrogen-saturated single-wall and multiwall nanotube samples studied in [61, 62].

On the basis of the analysis done in Refs [10, 96] and by comparing the above facts, we can rightfully assume that process β in the single-wall nanotube and GNF samples studied in [94, 95], which provides for $\leq 40\%$ of the sorption capacity of these samples, corresponds to the dissociative–associative chemisorption process II, which, in particular, is characterized (see Ref. [10]) by an accompanying release of a small amount of hydrocarbons during the thermal desorption heating of the carbon material.

The data obtained in [94, 95] on the sorption capacity and the kinetics of process β in GNF and single-wall nanotubes are described quite well by the sorption isotherm and the thermodynamic and diffusion characteristics corresponding to chemisorption process II, as was done in the analytical reviews in Refs [10, 97] for the experimental data in [12, 14, 61, 96].

Process β (II) can be related to the observed [see item (6)] release of hydrocarbons by single-wall nanotubes [95] subjected to prolonged (compared to the duration of the thermaldesorption heating done in [12, 14, 61, 96]) multistage heating to 673 K (373 K for 3 hours, 473 K for 3 hours, and 673 K for 3 hours) in a vacuum. It must be borne in mind here that the energy $-\Delta H_{(12)II} \approx 570$ kJ mol⁻¹ (characteristic of chemisorption process II) of desorption, or detachment, of two hydrogen atoms from a carbon atom in a zigzag edge position (see Fig. 8, model H) is much higher than the energy $-\Delta H_{C-C} \approx 485$ kJ mol⁻¹ of detachment of a carbon atom from two nearest carbon atoms. This suggests that as desorption process II runs, the formation of hydrocarbons may prevail within certain temperature and temporal ranges.

In this connection, it is useful to mention the experimental data in [98, 99] on the release of methane and molecular hydrogen by graphite materials, which can be interpreted as the manifestation of chemisorption process II. We also note that the accompanying (initiated) release of hydrocarbons cannot manifest itself in chemisorption process III, because for this process, the characteristic energy $-\Delta H_{(3)III} \approx 243 \text{ kJ mol}^{-1}$ of desorption, or detachment of one hydrogen atom from a carbon atom in a graphene layer in the material (see Fig. 8, model F*) is three times lower than the energy $-3/2 \Delta H_{C-C} \approx 730 \text{ kJ mol}^{-1}$ of detachment of a carbon atom from three nearest carbon atoms in a graphene layer. A similar situation can be shown to exist for chemisorption processes IV and I.

Based on the experimental facts discussed in this section [items (1)–(7)], we can compare (as was done in Refs [10, 17, 97]) process γ in the GNF and single-wall nanotube samples [94, 95], which provides not less than 60% of their sorption capacity, with chemisorption process III, which in certain conditions is described by the Sieverts sorption isotherm [Eqn (5a)]. This, in particular, agrees with the fact stated in item (1).

But this does not explain the fundamental fact [item (4)] of the anomalous increase (up to 40%) in the interplanar spacing between the graphene layers of the material [94, 95], because process III (as shown by the analysis in Refs [10, 17, 97] of the experimental data in [12, 14, 53, 96]) is characterized by a much smaller variation (by 2-7%) of this interplanar spacing for a similar adsorbate content.

Hence, there are reasons (including the results of the analysis in [52, 53, 60, 100, 101]) to believe that process γ in the GNF and single-wall nanotube samples in [94, 95]

corresponds to chemisorption IV (Table 1), which in certain conditions (as well as process III) can be described by the Sieverts sorption isotherm (5a).

Process IV, in contrast to process III, may lead to an anomalous increase in the interplanar spacing between the graphene layers in the adsorbent, because it has the highest energy of the C-H bond (models C and D in Fig. 8; Table 1) and is localized in the defective regions of the graphite lattice, at the edges of cluster (dislocation) loops of the interstitial type [53], etc., which may form in the material [94, 95] subjected to 'strained' hydrogen saturation under ultrahigh pressures (9 GPa).

The data in [94, 95] on the sorption capacity and the kinetics of process γ in GNF and single-wall nanotubes can be described quite well by the sorption isotherm and the thermodynamic and diffusion characteristics of chemisorption process IV, as we did in the analytical review in Ref. [10] for the experimental data in [52] on nanostructured graphite.

To establish the nature of process α , it is useful to estimate the diffusivity via Eqn (25). We can use the data in [94] on the release of ~ 0.15 mass% of hydrogen ((H/C)_{α} \approx 0.018) by GNF samples heated at the rate $v \approx 20$ K min⁻¹ from ~ 173 to 273 K. Assuming that the characteristic diffusion length (path) is of the order of the thickness of the GNF samples [94] and that the diffusion time (near the mean temperature $T_{\alpha} \approx 223$ K) is around $\Delta T_{\alpha}/v$, where $\Delta T_{\alpha} \approx 100$ K, we obtain the diffusivity $D_{\alpha} \approx 10^{-4}$ cm² s⁻¹ for process α .

This value of D_{α} is several orders of magnitude greater than the value of D_1 (at T_{α}) corresponding to the chemisorption process I and several orders of magnitude smaller than the gas diffusivity [68]. At the same time, it is close (in the order of magnitude) to the values of D^s and D^{def} (Sections 3.3 and 5.1, Tables 1 and 2) characteristic of the Van der Waals interaction, which indicates that the physical mechanism manifests itself in sorption process α . Estimates from Eqn (33) that use the experimental values of $(H/C)_{\alpha}$ and the acceptable values of the specific surface area ($\sim 100-300 \text{ m}^2 \text{ g}^{-1}$) for the samples used in [94] also point to the possibility of physical adsorption.

5.4 Polylayer physical adsorption in GNFs initiated by monolayer chemisorption

Between 1996 and 1999, sensational experimental data [12] (see Fig. 3, Chambers et al.) on a GNF-based superadsorbent (see Maeland's review in Ref. [7]) were presented at international conferences and published in scientific journals by a group of US researchers (Rodriguez, Becker, and others). So far, nobody has been able to reproduce the data described in Ref. [12], but they are examined and cited in reviews and research papers (see Refs [7–11]). The researchers who claim to have discovered this superadsorbent [12] do not consider their results erroneous, and have declared so, for instance, in their 2004 paper [13]. The researchers and was devoted to the study of hydrogen sorption by carbon materials.

As noted in Ref. [7], Becker 're-activated' the interest of researchers in 1972 by discovering graphite nanofibers 'anew.' It must also be noted that in recent years, Becker together with coworkers published a large series of fundamental papers and registered patents in this field.

At the same time, in discussing the problem of accumulating hydrogen, e.g., in the discussion that took place at the 9th International Conference 'Hydrogen materials science and chemistry of carbon nanomaterials' (Ukraine, 2005) [111], many researchers spoke of "expectations, delusions, and prospects," but also of "good luck, mistakes, and mystifications."

In this connection, we believe it is useful to analyze the data in [12], both critically and constructively, employing the novel methods developed in Refs [10, 17-25, 97]. The anomalously high experimental values of the sorption capacity of GNF samples (up to 40 mass% of hydrogen, $(H/C)_{\Sigma} \leq 8$ presented in [12] make this material a superadsorbent. The samples were saturated with hydrogen at \sim 11 MPa and 298 K for 24 hours. Lifting the high pressure and ageing the hydrogen-saturated samples for $\tau \ge 10$ min led to desorption of the larger fraction ($\sim 75\%$) of the adsorbate, i.e., to the release of $\sim 33 \text{ mass}\%$ of hydrogen by these samples (process αX , $(H/C)_{\alpha X} \leq 6$). Subsequent thermal desorption heating of the GNF samples up to ~ 1223 K at the rate $0.17 \,\mathrm{K}\,\mathrm{s}^{-1}$ from these samples revealed the presence of two high-temperature TPD peaks (β and γ in Fig. 6), which characterize the release of the remaining fraction ($\sim 25\%$) of the adsorbate [(H/C)_{$\beta+\gamma \leq 2$}].

The analysis of the experimental data in [12] carried out in Refs [10, 17–25, 97] shows that these TPD peaks β and γ are described fairly well by thermodynamic and diffusion equations and the characteristics corresponding to the respective chemisorption processes II and III. In other words, about 25% of the data obtained in [12] in 1999, referring to TPD peaks β and γ , agree fairly well with the data of other researchers (see Refs [14, 51-56, 61, 62, 94, 95]) gathered in the period from 1999 to 2005 (Table 1 and Figs 5 and 7). Hence, for at least 25% of the data in [12], we cannot speak of large (systematic) methodological errors, delusions, or mystifications, a fact not mentioned anywhere except in our series of papers [10, 17-25, 97]. We therefore believe that it is useful to consider the theoretical possibility, nature, and characteristics of the sorption process αX that prevails in GNF [12] and which obviously could satisfy the main technical requirements [3-5] that sorbent materials must meet if hydrogen is to be accumulated onboard a car.

To establish the nature of process aX in the GNF samples in [12], as in the case with process α in the GNF samples in [94], we estimate the corresponding diffusivity by using equations of type (22) and (25), which correspond to the fundamental diffusion law [68, 71]. We can use the data in [12] on the release of about 33 mass% of hydrogen $(H/C)_{\alpha X}\leqslant 6$ corresponding to the sorption capacity for process aX by the hydrogen-saturated samples kept at 298 K for $\tau \leq 10$ min. The remaining adsorbent (about 15 mass%) of hydrogen, $(H/C)_{\beta+\gamma}\leqslant 2)$ was released only after thermal desorption heating of the samples up to ~ 1223 K, which manifested itself in two high-temperature TPD peaks (β and γ in Fig. 6). Assuming that the characteristic diffusion path is of the order of the linear size of the GNF samples in [12] $(L \approx 0.5 \text{ cm})$ and that the diffusion time at 298 K is about 5 min, we obtain the diffusivity $D_{\alpha X} \approx 8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ for hydrogen in process αX .

As in the case of process α in the GNF samples in [94], the obtained value of $D_{\alpha X}$ is several orders of magnitude greater than the value of D_{I} (at 298 K) corresponding to chemisorption process I and is several orders of magnitude smaller than the gas diffusivity [68]. It is close (in the order of magnitude) to the values of D^{s} and D^{def} (Sections 3.3 and 5.1; Tables 1 and 2) characteristic of the Van der Walls interaction, which, obviously, points to the physical mechanism of sorption process αX .

The sensationally high sorption capacity of process αX [(H/C)_{$\alpha X \leq 6$}] is much higher than the maximum hypothetical chemisorption of hydrogen corresponding to the formation of CH₄ chemicomplexes. This points to the physical mechanism of sorption, which, theoretically at least, may be related to clusterization [31, 102], condensation [29, 30], and/ or polylayer intercalation [12, 103] of the adsorbate.

To a certain extent, a similar situation occurs in the case of the anomalous process (examined in Section 5.2) of unsaturable hydrogen sorption in single-wall nanotube samples examined in [77] (see Fig. 16) (up to the adsorbate concentrations $H/C \approx 1$ and $H/C_{exp}^{s} \approx 4$ at 80 K and 12 MPa), which is believed to be the cause of the disintegration or 'swelling' of bundles of single-wall carbon nanotubes.

A similar situation also occurs for the process of superadsorption of hydrogen in GNF samples studied in a series of experiments performed in [104] (the highest concentration reached in these experiments was $\sim 17 \text{ mass}\%$, with $H/C \approx 2.5 \text{ at} \sim 300 \text{ K}$ and 8 MPa). The process results in a very distinct nanostratification (of the intercalation nature) of the structure of GNF bundles (Fig. 20). These results may obviously be considered experimental proof of the mechanism of polylayer intercalation of hydrogen in GNF structures.

A certain substantiation of such a sorption process is provided by a series of theoretical works written in 2004 and 2005 by a group of researchers from Canada and Germany [105], who developed a new approach for accumulating hydrogen in graphene nanostructures.

On the other hand, using Monte Carlo simulation of the physical sorption of hydrogen molecules between the graphene layers of GNF samples (at 10 MPa and room temperature), some researchers (e.g., see Ref. [106]) have shown that it is impossible to interpret the anomalous adsorption data in [12] (process αX) within the standard models of molecular hydrogen-graphite interaction potentials.

In 2006, high-precision experimental data on the sorption capacity of activated carbon and GNF (≤ 0.6 and 0.3 mass%, respectively) saturated with hydrogen at room temperature and pressures up to 10 MPa were presented in [107]. The researchers noted that their values of the sorption capacity were close (in the order of magnitude) to the experimental data in [108] (0.77 mass%) and [109] (0.3 and 0.7 mass%; see also Fig. 3, [16]), but differed significantly (by two to three orders of magnitude) from the data in [12, 104] (see Fig. 20). Based on these facts, Blackman et al. [107] conclude (together with many other researchers) that the anomalous results in [12, 104] and those presented in Figs 3 and 4 may be caused by methodological factors.

In this connection, we emphasize that the data in [107] are close to the sorption data in [64] (see Figs 11 and 12), obtained by the same volumetric method combined with differential-pressure measurements. The results of the analysis in Section 5.1 show that the data of both groups of researchers, as well as the data of other well-known studies (e.g., see Refs [16, 84, 108, 109]), may correspond to the manifestation of another sorption process (physical-like monolayer chemisorption of type I, Table 1), in contrast to the anomalous data in [12, 104] examined in Section 5.4 (see Figs 6 and 20). Hence, the conclusion drawn in [107] (the 'diagnosis' made by many researchers) concerning the methodological reasons for the anomalies [12, 104] and Figs 3 and 4 do not seem to be sufficiently justified.



Figure 20. Micrographs of dehydrogenated GNF; the arrows indicate some of the formed slit-like nanopores [104].

It is also useful to consider the data in [61] (see Fig. 4) on the anomalously low sorption capacity and extremely slow thermal desorption of deuterium (with the activation energy $E_{\rm a}^{\rm des} \approx Q_{\rm II}$, Table 1) from single-wall nanotube samples deformed in a ball mill and saturated at room temperature and 0.08 MPa. The analysis of these data (see Section 4), which uses Eqns (22)-(24) and the characteristics for process II (Table 1), shows that the sorption process is limited by diffusion $(D_{\rm II})$ of deuterium over the distance $L \approx 20 \ \mu m$ (which is obviously of the order of the thickness of a single-wall nanotube sample), corresponding to chemisorption process II. Hence, the data in [61] cannot be contrasted with the data in [12, 104] on the anomalously high sorption capacity of the material $(H/C)_{\alpha X} \leqslant 6$ $(\leq 40 \text{ mass}\%)$ and the very fast (physical) kinetics of the desorption of hydrogen from the material $(D_{\alpha X} \gg D_{II})$, as was done in [8].

In the 2006 review [110], carbon nanomaterials (GNFs), as well as Mg-based materials, and complex light-metal hydrides are regarded as the most promising (main) adsorbents of hydrogen, capable of ensuring a very high sorption capacity and desorption kinetics; the researchers also noted the need for further fundamental studies in this field.

6. Conclusion

The critical and constructive analysis of the state and current level of studies on the nature, characteristics, and mechanisms of the interaction of hydrogen with graphite and related carbon nanomaterials demonstrates a real possibility of purposefully optimizing the synthesis, preconditioning, and hydrogen saturation of such materials with the goal of fabricating a superadsorbent of hydrogen (≥ 10 mass%) that would satisfy the technical requirements that sorbent materials must meet if hydrogen is to be accumulated onboard a car.

At the same time, we believe it is useful to broaden and deepen the discussion in scientific publications of the hydrogen accumulation problem (expectations, delusions, and prospects, but also good luck, mistakes, and mystifications) that took place at the 9th International Conference 'Hydrogen materials science and chemistry of carbon nanomaterials' [111].

The author is grateful to OK Alekseeva and OL Amosova for their help in making estimates and in preparing the review for publication.

This work was made possible by the financial support of the Russian Foundation for Basic Research (Grant 05-08-50222-a).

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