

SURFACE ENERGY OF OXIDES AND SILICATES

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Published data and the author's own data on the surface energy of hydrophilic oxides, silicates, and hydrophobic adsorbents based on them are reviewed. The prospects of using the combined Gibbs–Helmholtz–Young equation to obtain data on the surface pressure, heat of wetting, and wetting contact angle of hydrophilic and hydrophobic adsorbents are demonstrated. These data are used to estimate the thermodynamic characteristics of the surface and interfacial regions at the boundary between the materials and water. It is shown that the boundary layers of water close to the hydrophobic surfaces are more ordered while those close to the hydrophilic surfaces are less ordered than with liquid water.

Key words: *oxides, silicates, modification, hydrophobic adsorbents, surface and interfacial free energy, enthalpy, entropy.*

INTRODUCTION

Surface free energy (surface tension) is an important thermodynamic characteristic of the surface of liquids and solids. The theory and practise of the determination of surface tension for liquids have now been greatly developed. A fundamental monograph has been devoted to the subject [1]. In recent years investigators studying surface phenomena at a liquid–gas interface have concentrated their efforts on the nonequilibrium (dynamic) surface tension of solutions of surfactants, water-soluble polymers, and biomolecules [2, 3], the equilibrium surface tension of solutions of surfactants and their mixtures in the presence of electrolytes [4, 5], and the structure of the surface layer of pure liquids and their solutions (e.g., see [6–8]). In connection with the latter papers on finding correlations between the surface tension and its temperature coefficient and the volume characteristics of the liquids themselves have appeared [9].

The measurement of surface free energy (thermodynamic surface tension) and the interpretation of the results become considerably more complicated in the transition from liquids to solids. The reason for this is the presence in the samples of impurities local, as is known [10], in the surface layer, its roughness, and the presence of vacancies and dislocations, which change the structure of the crystals. Moreover, for solids in contrast to liquids under equilibrium conditions the surface free energy σ (the thermodynamic surface tension) and the mechanical surface tension γ do not as a rule coincide in value, as was first mentioned by Gibbs [11]. He stressed that the work expended on the formation of unit surface of a solid (its surface free energy) cannot be expressed in terms of the surface tension. This last property is determined by the work used in stretching the surface. The formation of a new surface or the stretching of an existing surface in the case of liquids involves the escape of additional atoms or molecules from the volume into the surface layer. As a result for liquid media under equilibrium conditions $\sigma = \gamma$.

Stretching of the surface of solids is usually accompanied not by an increase in the number of atoms or molecules on the surface, as in the case of liquids, but by a change in its deformation state. The stresses that appear here in the surface layer

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are relieved to a large degree on account of the appearance of vacancies at the surface of the crystal faces or of dislocations in its surface layers [12, 13].

The surface tension of an isotropic solid γ and its specific surface free energy σ are related by the familiar equation [14, 15]:

$$\gamma = \frac{d(\Sigma F_s)}{d\Sigma} = F_s + \Sigma \frac{dF_s}{d\Sigma} = \sigma + \Sigma \frac{d\sigma}{d\Sigma} \quad (1)$$

where F_s is the isochoric-isothermal potential of unit surface area, i.e., the specific surface free energy σ ; Σ is the area of the surface. For liquids the last term of this equation is equal to zero, and for solids it can be greater or less than σ in value [1, 16].

Theoretical calculations showed that γ is several times larger than σ for the ionic crystals of certain salts and oxides [17]. At the same time for molecular crystals and metals $\gamma/\sigma = 0.6-0.3$ [1]. For metals the differences between γ and σ from the standpoint of their derivatives with respect to electric potential can be detected experimentally by the estance method [18].

Because of the complexity of the experimental and theoretical determination of the surface free energy of solids there have been comparatively few such investigations, and they are often tentative in nature. There have been even fewer reviews on the subject. Among them attention must be drawn to a publication of more than 30 years ago [17], in which theoretical and experimental data on the surface free energy and surface tension of the ionic crystals of salts and oxides were presented. In [1] most attention was paid to a critical analysis of procedures for the determination of σ for solids and less attention to the results obtained by them.

In a comparatively recent review [19] in a section devoted to the surface energy of silicas most attention was paid to the dispersion component of the surface free energy of the materials. Unfortunately, the results from comprehensive investigation of the energy characteristics of the surface of silicas and other solids by adsorption and contact and immersion wetting methods were not mentioned. Precision measurements of the forces of adhesion between the modified surfaces of glass (an analog of silica) and mica, which were used to calculate σ_s and other thermodynamic characteristics of these materials (see below), have also not been analyzed.

From the foregoing it follows that the present review has to be concerned mainly with analysis of specific experimental data obtained by the various methods on the surface free energy of solids in a vacuum at the interface with water and other liquids without any detailed discussion of the experimental procedures. The latter can be found in other publications [1, 12, 13, 17].

This review will mostly discuss the thermodynamic surface characteristics of the initial and modified forms of quartz, amorphous silicas, glasses, and layer silicates and graphite and graphitized carbon black having similar applications. These materials are widely used in adsorption, chromatography, and heterogeneous catalysis and as fillers for polymers. A knowledge of their surface characteristics is therefore important for specialists working in the appropriate fields of science and technology.

Silicas and silicates are materials with a high-energy surface ($\sigma > 100-150 \text{ mJ/m}^2$), whereas their organic derivatives are materials with a low-energy surface ($\sigma < 100-150 \text{ mJ/m}^2$). Methods for the determination of σ and γ for solids with high-energy and low-energy surfaces differ in many respects. The respective subjects are therefore discussed in separate sections.

LOW-ENERGY SURFACES OF THE ORGANIC DERIVATIVES OF OXIDES AND SILICATES

Solids with low-energy hydrophobic or hydrophilic-hydrophobic surfaces mostly include polymers. Investigations of their surface free energy have featured widely in the literature (e.g., see [20-26]). This is explained not only by the great practical significance of the polymers but also by the existence of a whole series of semiempirical and empirical equations, which make it possible to determine the value of σ by measuring the contact angles θ with one or several liquids. Moreover, the σ and γ values for the low-energy surfaces are close [1], and this also facilitates researches on determination of the surface energy of the polymers. In the present work data on the surface energy of certain polymers and primarily

polytetrafluoroethylene (Teflon), which has a highly hydrophobic surface, will only be used for the purposes of comparison with the main subjects of the investigations – modified oxides and silicates.

In the last quarter of the last century in three leading colloid chemistry laboratories experimental methods were developed for determination of the forces of interaction (linkage or adhesion) between spheres, crossed by threads or cylinders of low-energy solids, in air, water, and dilute aqueous solutions of electrolytes. This made it possible to determine σ_S and σ_{SL} for the modified surfaces with great reliability. Thus, according to Shchukin et al. [27], for previously methylated glass spheres σ_S measured in air amounted to 22 mJ/m². This value agrees well with the surface energy of polyethylene determined from data on its contact wetting with water $\sigma_S = 26.1$ mJ/m² [22].

Later the same group of authors developed a procedure for measuring the forces of adhesion between solids crossed by threads [28]. The force of adhesion of two identical threads (spheres) is related to the surface free energy by the simple equation, proposed by Deryagin [29, 30]: $F = 2\pi R\sigma$, where R is the radius of the thread (sphere). In [31] this method was used to determine the free energy of interaction of crossed acetylcellulose fibers in water ($U \approx 90$ mJ/m²) and aqueous solutions of tetrabutylammonium iodide ($U = 30-40$ mJ/m²). The obtained results correspond to the surface free energy at the acetylcellulose–water interface (an aqueous solution of the surfactant) $\sigma_{SL} \approx 45$ mJ/m² (15-20 mJ/m²).

The forces of interaction between bent plates of muscovite, modified with cetyltrimethylammonium cations, in air, in water, and in dilute solution of NaCl and KBr were studied by the crossed cylinder method [30, 33, 34]. The contact angle of modified muscovite with an aqueous solution of cetyltrimethylammonium bromide ($8 \cdot 10^{-4}$ M) was measured in parallel ($\sigma_{LV} = 40$ mJ/m²). With the obtained data $\sigma_{SV} = 27$ mJ/m², $\sigma_{SL} = 22$ mJ/m², and $\theta = 64^\circ$ it was possible for the first time to confirm the accuracy of Young's equation [35]:

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta. \quad (2)$$

The authors in [36] drew attention to the fairly small contact angle $\theta = 64^\circ$ obtained in [30, 33, 34], although such an angle is typical of glass that has been modified successively with titanium dioxide and trimethyloctadecylammonium chloride [13]. The contact angle for octadecylammonium kaolinite at the interface with water vapor and air, calculated from data on the specific heat of wetting q and the surface pressure of the adsorbed aqueous film π , amounts 56°-71° and 67°-80° respectively, depending on the amount of cation-active modifier introduced onto the surface of the kaolinite in relation to the cation-exchange capacity of the mineral [37, 38].

The low value of the angle θ in the experiments [30, 33, 34] is most likely due to the presence of a hydrophilic center (the quaternary nitrogen atom), where the positive charge is concentrated at the bonds with the carbon atoms, in the modifier [39]. It is not impossible, however, that the low value of θ is also due to incomplete replacement of the initial cations K^+ on the outer surface of the muscovite plate by the long-chain organic cations.

Using the more long-chain dimethyloctadecylammonium bromide as modifier and adding the Langmuir–Blodgett modification technique to their arsenal, the authors of [36] obtained the thermodynamic characteristics $\sigma_{SV} = 27$ mJ/m² and $\sigma_{SL} = 34$ mJ/m², where L is distilled water and $\theta = 94^\circ$, for the modified muscovite. Similar results were obtained during study of the forces of adhesion between plates of muscovite modified with dicetyldimethylammonium acetate: $\sigma_{SL} = 28-36$ mJ/m², $\theta = 95^\circ$ [40]. Substitution of the values $\sigma_{SV} = 27$ mJ/m² and $\sigma_{SL} = 34$ mJ/m² in Young's equation (2) gives the contact angle $\theta \approx 95^\circ$, which coincides with the experimental value.

The conditions for the modification of muscovite given in [36] make it possible to suppose that the authors had obtained a hydrophobic material, on the surface of which the organic cations were chemisorbed together with the neutral amines. The joint sorption of the cationic and neutral forms of a modifier with more than ten carbon atoms in the alkyl chain is a characteristic feature of interaction that is superequivalent in relation to the cation exchange capacity between cationic surfactants and layer-type silicates [41, 42].

The spectral data in [39] show that long-chain organic cations form stable associates with neutral amines. This leads to a decrease in the positive charge at the hydrophilic center of the cationic form and, consequently, to an increase in the hydrophobicity of the modifying layer, which to judge from the size of the contact angle the authors of [36] observed in their experiments.

It is usual to compare the σ_{SL} values of solids modified by organic substances with the surface interfacial energy at the saturated hydrocarbon–water interface: $\sigma_{HW} \approx 50 \text{ mJ/m}^2$ [30]. The presence of positive charges at the hydrophilic centers of cationic modifiers sorbed by muscovite leads to $\sigma_{SL} < 50 \text{ mJ/m}^2$. However, the value $\sigma_{SL} = 11 \text{ mJ/m}^2$ obtained in [33, 34] is substantially smaller than the value $\sigma_{SL} = 34 \text{ mJ/m}^2$ [36]. This fact is also explained by the increased charge at the hydrophilic centers of the sorbed cationic modifiers compared with the typical charge of sorbed cation–amine associates.

Young's equation contains four variables, two of which, i.e., the surface energy of the wetting liquid σ_{LV} and the contact angle θ , can be determined reliably by modern methods. However, complicated experimental procedures are necessary to determine the surface energy of a solid σ_{SV} and the interfacial surface energy at its interface with the wetting liquid σ_{SL} (e.g., see [28, 32]). A whole series of semiempirical and empirical equations have therefore been proposed over the last 40-50 years for the calculation of these characteristics. Among them the equation of Girifalco and Good [43-46] has been widely used.

These authors started from the perfectly reasonable assumption that the rule of the geometric mean for the energy of mixed (AB) interactions, $E_{AB} \sim (E_{AA}E_{BB})^{1/2}$, which has been widely used in the familiar Hildebrand theory of regular solutions [47], holds perfectly well for nonspecific interactions in a system consisting of the low-energy surface of a solid and a wetting liquid. The equation of Girifalco and Good

$$\sigma_{SL} = \sigma_S + \sigma_{LV} - 2\Phi(\sigma_S\sigma_{LV})^{1/2} \quad (3)$$

is largely reminiscent of the equation for the energy of mixing used in the theory of regular solutions [47, 48].

In Eq. (3) the coefficient Φ , called the interaction parameter, characterizes a specific system. For ideal liquid–liquid systems, having spherical molecules of equal size, $\Phi \approx 1$. However, of more than 130 investigated pairs of liquids only 15% had $\Phi = 0.95-1.05$, while the value of Φ as a whole varied between 0.32 and 1.15 [43].

The following equation was used to calculate Φ [43]:

$$\Phi = \frac{\sigma_S + \sigma_{LV} - \sigma_{SL}}{2(\sigma_S\sigma_{LV})^{1/2}}. \quad (4)$$

Substitution of the experimental values $\sigma_S = 27 \text{ mJ/m}^2$ and $\sigma_{SL} = 34 \text{ mJ/m}^2$ for modified muscovite, obtained in [36], in this equation gives $\Phi = 0.74$, which we used in [49] to calculate the thermodynamic characteristics of modified silica (layer silicates)–water systems. It is significant that the obtained value practically coincides with the interaction parameter $\Phi = 0.77$ for the benzene–water system [50].

In practise Eq. (3), in conjunction with Young's equation (2), is usually employed. Assuming that $\Phi = 1$ and $\pi = \sigma_S - \sigma_{SV}$ it is possible to obtain [13]:

$$\cos \theta = -1 + 2(\sigma_S\sigma_{LV})^{1/2} - \frac{\pi}{\sigma_{LV}} \quad (5)$$

where π is the surface pressure of the film of adsorbed water:

$$\pi = -\Delta F = \frac{RT}{\Sigma} \int_0^{P_s} a d \ln p. \quad (6)$$

In Eq. (6) ΔF is the change in surface free energy during contact between the degassed surface of the solid and the saturated water vapor, and a is the magnitude of the adsorption, measured in moles and referred to unit mass of the adsorbent.

The method of Girifalco and Good undoubtedly initiated researches on the determination of contact angles and surface energy for polymers. Analysis of the results can be found in a whole series of publications (e.g., see [13, 22]).

The use of the Girifalco–Good method is complicated somewhat by the need to determine the correct coefficient Φ . The method proposed by Zisman [51] for determination of the critical surface tension has therefore been quite widely used. In this method the $\cos \theta(\gamma_{LV})$ relationship is obtained experimentally for various wetting liquids on the same low-energy surface and is subsequently extrapolated to $\cos \theta = 1$. The corresponding value of γ_{LV} represents the critical surface tension γ_{cr} . If $\sigma_{LV} > \sigma_{SV}$, which is typical of the low-energy surfaces of solids, the following equation holds:

$$\cos \theta \sim 2\sigma_{SV}/\gamma_{cr} - 1. \quad (7)$$

It follows from this equation that $\sigma_{SV} = \gamma_{cr}$ if $\cos \theta = 1$.

A detailed analysis of Zisman's method and numerous examples of its application were given in [52]. In the recently published paper [25] the critical surface tension method was compared with the Neiman equation of state [1, 23]. It follows from these publications that this method together with numerous semiempirical approximations can be used to evaluate σ_{SV} for low-energy surfaces. However, to determine the surface free energy of solids it is necessary to take account of the surface pressure of the adsorption film π : $\sigma_S = \sigma_{SV} + \pi$. The authors of [25] also demonstrated that more reliable results in the determination of the critical surface tension are obtained if the linear $\cos \theta(\sqrt{\sigma_{LV}})$ relation is used.

In the Girifalco–Good method all deviations from the dispersion character of interaction between the solid matrix and the wetting liquid are taken into account by the interaction parameter Φ . The difficulties in its determination forced the investigators to seek other methods for the determination of σ_{SV} and σ_{SL} . It was proposed to separate the surface free energy into dispersion and nondispersion components (the Fowkes [53] and Owens–Wendt [54] methods) and also into electron-donating, electron-withdrawing, and van der Waals–Lifshits components (the method of Van Oss et al. [55]).

A critical analysis of the Fowkes and Owens–Wendt methods can be found in [20, 56, 57]. A major disadvantage of these methods is the inapplicability of the additivity rule during determination of the total surface energy of the solid from its dispersion and polar components. In any case, treatment of the experimental data on the forces of interaction between the modified surfaces of muscovite plates in [58] showed an undoubted advantage for the Neiman method.

Another disadvantage of the method proposed by Van Oss et al. is the use of the additivity rule. A comparative assessment of the Owens–Wendt [54] and Van Oss [55] methods with a critical analysis of the obtained results was given in the exhaustive paper [59]. A general conclusion that follows from this publication is that reliable values of the surface free energy, obtained by methods using the additivity approximation, can only be obtained for nonpolar or weakly polar solids (of the polymethylmethacrylate type) with observance of the necessary requirements for the wetting liquids. In the Van Oss method [55], for example, one wetting liquid must be apolar, while two must, first, be monopolar and, second, have different polarity.

The Fowkes method [53] was used to determine the free surface energy of samples of montmorillonite modified by alkylammonium cations [60]. It is interesting that the contact angles on their surface were measured at the line of contact between the solid and two liquid phases: Saturated hydrocarbon–water. The obtained angles were used to calculate the dispersion (D) and polar (P) components of the surface energy. Thus, for the octylammonium sample of the mineral with zero moisture content $\sigma_S = \sigma_S^D + \sigma_S^P = 27.1 + 12.0 = 39.1 \text{ mJ/m}^2$, and for dedecylammonium montmorillonite $\sigma_S = 21.2 + 2.4 = 23.6 \text{ mJ/m}^2$. The obtained values are close to the value $\sigma = 30\text{--}40 \text{ mJ/m}^2$ characteristic of polymers with a low-energy surface [22, 52] or the value $\sigma = 27 \text{ mJ/m}^2$ determined experimentally for muscovite modified with cationic surfactants [33, 36]. The authors [60] took account of the value of π by calculating the σ values for samples of organomontmorillonites containing adsorption water, and this made it possible to obtain coinciding results in the determination of σ for the dry and moist surfaces of the sorbents.

While calculating the surface energy of kaolinite modified with dodecylammonium chloride on the basis of the contact angles for wetting of the sorbents with glycerol and diiodomethane the authors of [61] obtained a reliable decrease in the dispersion component of the surface energy (from 39–40 to 25 mJ/m^2) with increase in the degree of modification from 0.125 to 1.0 and together with this an anomalous increase of the polar component from 15 to 24 mJ/m^2 .

In our opinion, the last result may be due to the different orientation of the particles of kaolinite modified to various degrees in the compressed tablets. With a degree of modification close to unity the fully hydrophobized side faces of the kaolinite particles tend as a result of the unique hydrophobic interaction [30, 62] to concentrate inside the tablet, while on its

TABLE 1. The Contact Angles and Temperature Coefficients for the Wetting of Solid Surfaces with Water according to [69, 70]

θ_a , deg	θ_v , deg	$d\theta_v/dT$, deg/K
22 ± 2	19 ± 3	+0.458
31 ± 2	24 ± 1	+0.306
44 ± 2	33 ± 2	+0.257
64 ± 3	53 ± 3	+0.170
72 ± 2	60 ± 2	+0.006
77 ± 1	69 ± 3	+0.003
85 ± 3	75 ± 2	0
103	93	-0.01
108	98	-0.02

surface the kaolinite particles are mainly concentrated with their basal faces, which are weakly affected by the modifying agent. Detailed information on the distribution of the exchange centers on the side and basal faces of the kaolinite crystals can be found in the monograph [63].

Detailed investigations by Adamson [13] showed that it is not possible to disregard the surface pressure of the adsorbed film of the wetting liquid π with any semiempirical calculations of the surface free energy of solids with a low-energy surface, irrespective of whether water [64] or hydrocarbons [65] are used. It is also necessary during determination of the thermodynamic characteristics of the surface of solids to combine the results from determination of π with the heats of wetting (immersion) q . It is with the use of data on q and π in [66] that the energy of adhesion was determined for a series of hydrocarbons from hexane to hexadecane on Teflon; it amounted to $W = 32 \text{ mJ/m}^2$.

The surface characteristics of solids are described almost completely by the thermodynamically rigorous equation, with three parameters π , q , and θ , first obtained in [67] by combination of the Gibbs–Helmholtz and Young equations:

$$q = \pi - T \frac{d\pi}{dT} + \sigma_{LV} \cos \theta - T \frac{d(\sigma_{LV} \cos \theta)}{dT}. \quad (8)$$

After differentiating the last term of Eq. (8) and transformations we obtain [68]:

$$q = \pi - T \frac{d\pi}{dT} + U_{LV} \cos \theta - T \sigma_{LV} \sin \theta \frac{d\theta}{dT} \quad (9)$$

where U_{LV} is total surface energy of the wetting liquid at its interface with the vapor. In the case of water $U_{LV} = 118.5 \text{ mJ/m}^2$ at 20°C .

Equations (8) and (9) in the full form have not been used in the scientific literature on account of the difficulties involved in the determination of the temperature coefficients $d\pi/dT$ and $d\theta/dT$. The authors of [69] carried out a scrupulous investigation on determination of the coefficients $d\theta/dT$ in the range of $\theta_v = 19^\circ$ – 75° for the wetting of glass modified to various degrees by treatment with soda. The results obtained in this work, supplemented by data for the polyethylene–water ($\theta_a = 103^\circ$) and polypropylene–water ($\theta_a = 108^\circ$) systems [70], are presented in Table 1.

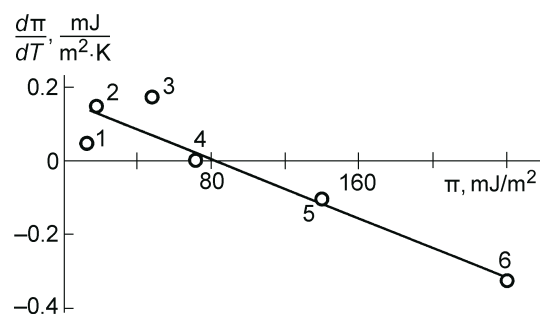


Fig. 1. The dependence of the thermal coefficient of surface pressure on the surface pressure: 1) Polyethylene; 2) graphitized carbon black; 3) stearic acid; 4) silver iodide; 5) α -iron oxide; 6) Ca-kaolinite.

In Fig. 1 the $d\pi/dT(T)$ curve, presented in [68, 71], is supplemented by results obtained during the sorption of water on stearic acid and polyethylene [64]. Analysis of the results presented in Table 1 and Fig. 1 shows that the temperature coefficients change sign, passing through zero at $\theta_v = 75^\circ$ and $\pi = 85 \text{ mJ/m}^2$. This characteristic of the temperature coefficients was used to separate nonporous and wide-pore adsorbent into hydrophilic and hydrophobic [71].

It is known that the contact angle of polytetrafluoroethylene (Teflon) during wetting with water varies from 112° to 98° depending on its purity [13]. Plasma treatment of Teflon and its amorphous modification Teflon AF improves the wettability of these materials with water [72]. Nevertheless among materials with a smooth (polished) surface Teflon is usually considered extremely hydrophobic. Its average surface energy, calculated using various semiempirical approximations, is estimated as 18.3 or 22.0 mJ/m^2 depending on whether the surface pressure is disregarded (the first figure) or taken into account [65]. Amorphous Teflon AF is characterized by the similar value $\sigma_s = \sigma_{sv} + \pi = 13.5 + 8.8 = 22.4 \text{ mJ/m}^2$ [26].

Films of polyfluoroalkylsilanes deposited on glass and quartz plates are characterized by even smaller values of σ . With increase in the length of the fluorocarbon chain the value of σ_s for the films, calculated by means of an equation similar to Eq. (5), decreases from 17.9 to 10.5 mJ/m^2 [73].

Aggregation of the nanoparticles of polytetrafluoroethylene or polypropylene deposited on glass or quartz plates leads to the appearance of nanodimensional irregularities in the deposited phase, and this increases the contact angle of water to $\theta = 145^\circ$ - 170° [74]. A formal assessment of the surface free energy of the deposited irregular polymer phase on the basis of data on the hysteresis of the contact angle [75] leads to $\sigma_s = 6$ -7 mJ/m^2 [74].

The increase of θ for the microinhomogeneous surfaces is due to the presence of air in the surface nanopores and is not directly related to the creation of truly superhydrophobic materials (see below). This effect has been known for a long time. Thus, during the wetting of a stearic acid crystal with water $\theta = 95^\circ$. Stearic acid powder, however, deposited on a substrate has $\theta = 160^\circ$ [76]. Theoretical analysis of the dependence of the contact angle on the microrelief or roughness of the surface was undertaken by Deryagin as far back as 1946 [77].

The results presented above give reason to consider that bulk samples or films of Teflon with a smooth surface provide a suitable subject of comparison during study of the thermodynamic characteristics of the surface of hydrophobized oxide and silicate sorbents.

Another subject of comparison during the study of hydrophobized sorbents is graphite and its derivatives. In [78, 79] the surface free energy of graphite was determined experimentally by the cleavage method $\sigma_s = 127$ -135 mJ/m^2 . The surface pressure $\pi = 21 \text{ mJ/m}^2$ [82] of a water film adsorbed on graphite, determined by means of Eq. (9) with $\sigma_s = 127 \text{ mJ/m}^2$, $\theta_a = 82^\circ$ [80], and $q = 23 \text{ mJ/m}^2$ [81], agrees well with the value $\pi = 19 \text{ mJ/m}^2$ determined by Harkins [83].

In [84] an interesting method was proposed for the determination of σ_{SL} for carbon materials on the basis of NMR measurement of the energy expenditures on the freezing of a water film in contact with the surface of a carbon material. The

TABLE 2. The Physicochemical Characteristics of the Hydrophobic Sorbents

Sorbent	Σ , m ² /g	a_m , mmol/g	ω , nm ²	π , mJ/m ²	q , mJ/m ²	θ_a , deg	θ_v , deg
Teflon	–	–	–	8.8	–46	108	98
C ₆ F ₁₃ -Silochrom	98	0.065	2.50	10.6	15.3	90	80
C ₆ F ₁₃ (CH ₃) ₃ Si-Silochrom	99	0.045	3.65	6.0	12.1	91	81
PEHS-Silochrom	45	0.10	0.75	27	7.7	96	86
RNH ₃ ,RNH ₂ -Kaolinite	42	0.24	0.29	120	185	80	71
Graphite	–	–	–	21	23	82	72

authors have only to increase the reliability of the obtained results for the values obtained by the NMR method to be close to the value of $\sigma_{SL} = 96$ mJ/m² [82], calculated by the rigorous Young's equation [see Eq. (2) of the present work].

Carbon fibers, produced from polyacrylonitrile and viscose fibers, petroleum pitch, etc., are now widely used for the reinforcement of plastics. High-strength carbon fibers have substantially lower surface energy: 53-57 mJ/m² estimated in [85], 29-49 mJ/m² according to data in [86]. Quite naturally the reduced σ_s values secure better compatibility between the carbon fibers and the polymers during the creation of composite materials reinforced with carbon fibers for various purposes.

Diamond-like and tetrahedral amorphous carbon have recently attracted the continuous attention of research workers in connection with their use as artificial implants, developed antiseptics, etc. In [87] the surface characteristics of these modifications of carbon, previously deposited on steel plates, were studied. The contact angles of such products with water ($\theta = 50^\circ$ - 68°), diiodomethane, and ethylene glycol were measured. These data were used to determine their surface free energy ($\sigma_s = 35$ - 50 mJ/m²) and its various components using almost all semiempirical approximations. It was shown that σ_s decreased regularly with increase in temperature in the range of 20-95 °C.

It is also necessary to mention the successful attempt at chemical modification of finely ground graphite with *n*-alkylamines and alkyltriazines [88]. The contact angle of these organic derivatives of graphite with water increased from $\theta_a = 43^\circ$ for the initial oxidized sample to 88° - 98° for products with grafted alkylamines and 97° - 124° for graphite with grafted butyl- and hexadecyltriazine. The last sample can be regarded as an example of the so-called superhydrophobic adsorbents with a contact angle with water in the order of $\theta_a = 160^\circ$ - 170° . Such aerosilica gels were obtained in methanol as medium with methyltrimethoxysilane as precursor [89]. Unfortunately, the authors do not cite the original papers by Prof. I. B. Slinyakova on the production and properties of the extremely hydrophobic xerogels of polymethylsiloxane, polyhydridosiloxane, and other organosilicon sorbents carried out at the beginning of the sixties of last century at the L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Slinyakova summarized these investigations in the monograph [90].

In our researches on the surface energy of solids in addition to Teflon [49, 91] and graphite [82], we used the following sorbents: Silochrom modified with tridecylfluoroalkyl radicals (C₆F₁₃-Silochrom) and also with additionally silanized trimethylchlorosilane [C₆F₁₃(CH₃)₃Si-Silochrom] [92]; Silochrom modified with polyethylhydridosiloxane (PEHS-Silochrom) [49]; structurally imperfect Glukhovsk kaolinite modified with an excess of octadecylammonium bromide in relation to the cation-exchange capacity (RNH₃,RNH₂-kaolinite) [37, 38, 49]. The physicochemical characteristics (the specific surface Σ , the BET capacity of a nominal monolayer a_m , the molecular area of water sorbed in the nominal monolayer ω , the surface pressure of the adsorbed water film π , the specific heat of wetting with water q , the contact angle with water in air θ_a and in saturated water vapor θ_v) of the sorbents are given in Table 2.

The negative heat of wetting of Teflon that we obtained by means of Eq. (9) (see Table 2) was confirmed by experiment [44, 93] and by calculations [44]. Silochrom with grafted tridecylfluoroalkyl radicals has a surface similar to Teflon. However, a small quantity of vicinal OH groups from the initial silica surface unaffected during modification remains on the surface of

TABLE 3. The Thermodynamic Surface Characteristics of Hydrophobic Sorbents

Sorbent	σ_s , mJ/m ²	H_s , mJ/m ²	S_s , mJ/(m ² ·K)	σ_{SL} , mJ/m ²	H_{SL} , mJ/m ²	S_{SL} , mJ/(m ² ·K)
Teflon	17.6	20.8	0.011	18.9	66.8	0.16
C ₆ F ₁₃ -Silochrom	31.6	70.9	0.13	8.4	55.6	0.16
C ₆ F ₁₃ (CH ₃) ₃ Si-Silochrom	27.8	67.5	0.14	6.2	55.4	0.17
PEHS-Silochrom	39.5	63.0	0.080	5.0	55.3	0.17
RNH ₃ ,RNH ₂ -Kaolinite	161	365	0.695	17.4	180	0.55
Graphite	127	155	0.096	96	132	0.12

the modified Silochrom [92]. Moreover, the grafted fluoroalkyl radicals do not remain inert when the sorbents are wetted with water. They rise above the surface, making the previously physically screened isolated OH groups of the silica accessible to the water. These two reasons lead to the final positive heat of wetting of the modified sorbents with water.

At high relative pressures $p/p_s > 0.8$ the orientation of the grafted fluoroalkyl radicals in relation to the surface of the silica changes. This does not make it possible to determine reliably the contribution from additional hydration of the silanol groups on the initial silica surface to the value of π and explains the smaller values of the contact angles calculated for the fluoroalkyl derivatives of silica (Table 2) compared with the contact angle with water determined experimentally for quartz capillaries modified with fluoroalkyl radicals [94].

Under the influence of the adsorbed water the long-chain cationic surfactants change their orientation in relation to the surface even at $p/p_s = 0.3-0.5$ [38]. This affects both the physicochemical and the thermodynamic surface characteristics of the modified kaolinite (for greater detail, see [49]).

While coating the silica with a fairly thick modifying layer (4-6 nm), polyethylhydrosiloxane nevertheless has continuity breaks in its structure, making a small part of the initial surface of the silica accessible to the water molecules [95]. However, comparison of our experimentally determined [49] contact angle for PEHS-silica and water with the angles presented in [96] for a silanized silicon/silicon dioxide substrate indicates that the PEHS-silica is highly hydrophobic.

The excess surface (with subscript S) and interfacial (with subscript SL) thermodynamic characteristics (free energy σ , enthalpy H , and entropy S) were estimated for the modified sorbents on the basis of the π , q , and θ_V values presented in Table 2, using the Girifalco–Good molecular theory of wetting [43-45]. The detailed procedure for calculation of the thermodynamic characteristics was described in [49]. The results are presented in Table 3.

For graphite experiment gives $\sigma_s = 127-135$ mJ/m² and $H_s = 155$ mJ/m² [79]. This makes it possible to determine the remaining thermodynamic values reliably [82]. The interaction parameter for the graphite–water system, calculated by means of Eq. (4), is $\Phi = 0.45$. To determine Φ it is also possible to use the following equation [44]:

$$H_s = \frac{(H_{LV} - h)^2}{4H_{LV}\Phi^2} \quad (10)$$

where $H_{LV} = U_{LV}$, and $h = -q$ is the specific heat of immersion. Calculation by this equation gives $\Phi = 0.52$.

Thus, the presence of strong hydrophilic centers, such as carboxyl, ketone, and other groups of acidic and basic character [97, 98], on the surface of largely hydrophobic graphite reduces the interaction parameter to $\Phi = 0.5$ compared with the value $\Phi = 0.74$ characteristic of the hydrophobized sorbents.

The existence of experimental values of σ_S and H_S for graphite makes it possible to obtain the ratio $\sigma_S/H_S = 0.87-0.82$, which is very close to the ratio $\sigma_S/H_S \approx 0.9$ proposed by Brunauer for the high-energy surfaces of solids [16]. The coefficient $f = \sigma_S/H_S = 0.45$ is recommended in [99]. It follows from Table 3 that for modified sorbents $f = 0.41-0.63$. Such a ratio is incorporated in the most semiempirical approaches, which are actually based on the theory of regular solutions of nonelectrolytes. This is favored by the values $f = 0.42-0.61$ for a series of liquids [100].

While being excessive in relation to the characteristics of the solid itself, the σ_S , H_S , and S_S values presented in Table 3 are positive according to the definition in [1]. As far as the σ_{SL} , H_{SL} , and S_{SL} values are concerned, they are excessive in relation to the wetting liquid and must be interpreted on the basis of the structure of the interfacial region [50]. Thus, for hydrophilic hydromica the negative value of S_{SL} indicates directly that the structure of the water in the region adjacent to its surface is more ordered than with liquid water (for greater detail, see below and also [49]).

The S_{SL} values for all the hydrophobic adsorbents presented in Table 3 are positive. This serves as evidence for the more ordered structure of the water in the interfacial region compared with liquid water and agrees with adsorption–calorimetric investigations of hydrophobized kaolinite [38]. In the cited work it was shown that the average molar entropy of the water adsorbed on this sample is higher than the entropy of liquid water.

HIGH-ENERGY SURFACES OF OXIDES AND SILICATES

There are hardly any theoretical calculations on the surface energy of silicates and oxides in the literature. Papers on the determination of σ_S by the cleavage of crystals and of H_S by the dissolution of the particles of high-energy subjects with various degrees of dispersion and known porosity therefore remain at the center of attention. The theoretical and experimental principles of these methods were set out in [1, 13, 101]. The first determination of σ_S by the cleavage method was by Obreimov as applied to mica-muscovite [102, 103]. The values that he obtained, $\sigma_S = 375 \text{ mJ/m}^2$ in air and $\sigma_S = 5000 \text{ mJ/m}^2$ in a high vacuum, were close to the results from successive determinations of σ_S for muscovite using improved procedures.

The high σ_S value of muscovite measured in a high vacuum is explained by electrification of the mica crystals as a result of electron transfer at the moment of splitting from the structural oxygen ion to the K^+ cation. The most accurate value of $\sigma_S = 480 \text{ mJ/m}^2$ for muscovite was obtained by Prof. M. S. Metsik at Irkutsk University under vacuum conditions ($p = 13.3 \text{ Pa}$) with continuous ionization of the residual air to neutralize the surface charges and with low cleavage rates ($\sim 0.02 \text{ cm/s}$) [104]. Theoretical determination of σ_S for muscovite using an electrostatic model and on the condition of equal distribution of the K^+ ions over the contacting surfaces led to the similar value $\sigma_S = 460 \text{ mJ/m}^2$ [104]. This value agrees better with experiment than the value $\sigma_S = 891 \text{ mJ/m}^2$ calculated in [105].

Data on determination of the surface free energy of muscovite as a result of cleavage of its crystals in dry air ($\sigma_S = 308 \text{ mJ/m}^2$), water vapor ($\sigma_{SV} = 183 \text{ mJ/m}^2$), liquid water ($\sigma_{SL} = 107 \text{ mJ/m}^2$), and hexane vapor and liquid hexane ($\sigma_{SV} = 271$ and $\sigma_{SL} = 255 \text{ mJ/m}^2$ respectively) have been widely published in the English literature [106]. Our experience in the investigation of muscovite and the structurally similar hydromica [49, 107] makes it possible to give preference to the results in [104] from determination of the surface free energy of muscovite under vacuum ($\sigma_S = 480 \text{ mJ/m}^2$) and in water ($\sigma_{SL} = 150 \text{ mJ/m}^2$).

It is interesting that determination of the surface enthalpy of calcium silicate tobermorite (a mineral close to layer silicates in structure) by Brunauer [108], using the solution method, gave $H_S = 450 \text{ mJ/m}^2$. In consideration of the relation $f = \sigma_S/H_S = 0.9$ [16], for tobermorite we obtain $\sigma_S = 405 \text{ mJ/m}^2$. These values can serve as a reference point in the determination of the surface energy of layer silicates.

The calculations of the surface energy of oxides and silicates based on preliminary measurement of the contact angles with various liquids are of little value on account of the presence of molecularly bound water on the surface of these hydrophilic materials. Ambiguity arises on account of the uncertainty as to the surface state (absolutely dry, fully or partially saturated with water vapor) to which the obtained results refer. This applies particularly to the data in [109], in which the surface energy of talc and illite (hydromica), as the sum of the various components of σ_S , was determined by the capillary rise method. In [110] it was nevertheless observed that the obtained σ values, calculated from data from measurement of the contact angles, refer to hydrated samples of kaolinite, while in [111] an attempt was even made to account for the partially hydrated state by

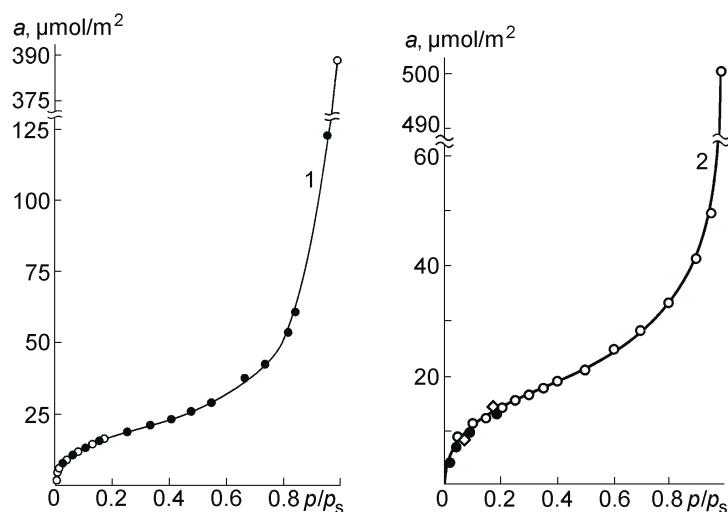


Fig. 2. The adsorption isotherms of water vapor on mica (hydromica) (1) and quartz (2). The various points correspond to the results of independent measurements.

incorporating the surface pressure of the adsorbed monolayer of water in the total value for the surface free energy of the kaolinite.

However, our experience shows that under real conditions the samples of layer silicates contain bound water in an amount corresponding the relative water vapor pressure $p/p_s = 0.5-0.55$ and not the value $p/p_s \approx 0.1$ typical of monolayer coverage [112]. Therefore, while applying the correct approach to the determination of σ_s for kaolinite, the authors of [111] obtained a low result.

In [113] a procedure involving measurement of the contact angle at the line of contact between a solid and two liquid phases (water and various nonpolar and weakly polar liquids) was used to determine σ_s . The low values $\sigma_s = 120 \text{ mJ}/\text{m}^2$ obtained in the experiment were due to the saturation of the muscovite with adsorption water after the introduction of a drop of water onto the surface of the mica under the layer of organic material.

An advantage of the procedure for determination of the surface enthalpy of sorbents based on measurement of their heats of wetting in three liquids (water, formamide, hexane) is the preliminary degassing of the sorbents under vacuum and bringing them into contact with the wetting liquid without access to air. By treating the results according to the theoretical approach of Van Oss et al. [55] it was possible to obtain reasonable values for the surface enthalpy of the sorbents [114, 115], i.e., H_S 535 for quartz, 294 for silica gel, and $144 \text{ mJ}/\text{m}^2$ for carbosil, which agree satisfactorily with the measurements of other authors (see below). There is, however, an objection to the authors' proposed ratio of 2.5-2.0 between H_S and σ_s ($f = 0.4-0.5$), which contradicts the experimental data for high-energy materials [16] and even graphite ($f \approx 0.9$) [79, 82].

The σ_s value for quartz was determined experimentally by splitting its crystals along two different planes: $\sigma_s = 410$ and $500 \text{ mJ}/\text{m}^2$, average $\sigma_s = 455 \text{ mJ}/\text{m}^2$ [116]. With $f = 0.9$, $H_S = 506 \text{ mJ}/\text{m}^2$, which is close to the data discussed above [114, 115].

The surface enthalpy of the hydroxylated surface of amorphous silica $H_S = 129 \text{ mJ}/\text{m}^2$, determined by the dissolution method [117], is only a little higher than the surface total energy of water $U_{LV} = 118.5 \text{ mJ}/\text{m}^2$. Dehydroxylation of amorphous silica increases H_S to $259 \text{ mJ}/\text{m}^2$. The difference ΔH_S between the siloxane and silanol surface represents the heat of hydroxylation $\Delta H_S = Q_\Gamma = 130 \text{ mJ}/\text{m}^2$. If this value is compared with the decrease in the concentration of hydroxyl groups during dehydroxylation (in the experiments of Brunauer et al. [117] $\Delta C \approx 4 \text{ OH}/\text{nm}^2$), it is easy to obtain the heat of hydroxylation of amorphous silica calculated per mole of OH groups $Q_\Gamma = 19.5 \text{ kJ}/\text{mol}$.

In [118] the heat of wetting of the siloxane sections on the surface of amorphous silica ($\sim 60 \text{ mJ}/\text{m}^2$) was determined from the decrease in the specific heat of wetting ($\Delta q = 50 \text{ mJ}/\text{m}^2$) and the average concentration of surface OH groups ($\Delta C = 2.8 \mu\text{mol}/\text{m}^2$) in the transition from silica gel to aerosil. The obtained value was close to the value of $50 \text{ mJ}/\text{m}^2$ presented in [119].

TABLE 4. The Physicochemical Characteristics of Hydrophilic and Hydrophilic-Hydrophobic Adsorbents

Sorbent	Σ , m ² /g	a_m , mmol/g	ω , nm ²	π , mJ/m ²	q , mJ/m ²	θ_a , deg	θ_v , deg
Hydromica	121	1.71	0.118	253	485	7	2
Quartz	–	–	0.133	215	430	8	3
Talc	5.1	0.055	0.154	130	195	83	73

The use of Eq. (9) for the joint analysis of π , q , and θ provided the basis of a new development in the study of the surface energy of solids, including hydrophilic oxides and silicates [68, 71]. Figure 2 shows the adsorption isotherms of water vapor on hydromica and quartz [49, 107, 120], in which the adsorption values are expressed in $\mu\text{mol}/\text{m}^2$. The surface pressures of a film of adsorbed water π , presented in Table 4 together with other physicochemical characteristics of the sorbents, were calculated on the basis of these isotherms. The data for talc, which as known [68] has a hydrophilic-hydrophobic surface, are given in the same table for comparison.

Published values for the surface pressure of a film of adsorbed water on quartz vary between $\pi = 120 \text{ mJ}/\text{m}^2$ [121, 122] and $307 \text{ mJ}/\text{m}^2$ [19, 123]. The value that we obtained (Table 4) is the average value $\pi = 215 \text{ mJ}/\text{m}^2$. Such a spread of the π values is due primarily to the different methods used for the determination of the adsorption isotherms of water on quartz (chromatography, gravimetry, or as in our case a combination of gravimetry and ellipsometry).

The accuracy of determination of π could, however, be checked if the heat of wetting of the adsorbent were measured in parallel. For this purpose we use the simplified Eq. (9), which can be applied to highly hydrophilic sorbents with small contact angles:

$$q = \pi - Td\pi/dT + U_{LV} \cos \theta_v. \quad (11)$$

For quartz it can be assumed to a first approximation that $\theta_v = 0$. From the curve presented in Fig. 1 for the quartz–water system we find that $d\pi/dT = -0.27 \text{ mJ}/(\text{m}^2 \cdot \text{K})$. The value of $q = 415 \text{ mJ}/\text{m}^2$ calculated by means of Eq. (11) almost coincides with the experimental heat of wetting of quartz presented in Table 4.

Evidence for the accuracy of the determination of π can also be obtained by using the method of analogies, i.e., by comparing the values of π and q for quartz with those for mica with hydrophilicity close to that of quartz, where the values of $\pi = 253 \text{ mJ}/\text{m}^2$ and $q = 485 \text{ mJ}/\text{m}^2$ were checked by using experimental data on the surface energy of mica σ_s under vacuum and at the boundary with liquid water σ_{SL} [104]. Calculation shows that the π/q ratios are similar both for quartz and for mica (see Table 4) and amount to 2.0-1.92. At the same time substitution of the value $\pi = 120 \text{ mJ}/\text{m}^2$, given in [122] for quartz, and the corresponding value of $d\pi/dT = -0.07 \text{ mJ}/(\text{m}^2 \cdot \text{K})$, obtained from the curve in Fig. 1, in Eq. (11) gives the calculated value $q = 260 \text{ mJ}/\text{m}^2$, which differs strongly from the experimental value $q = 383 \text{ mJ}/\text{m}^2$ [122].

From the values of q and π for talc it was possible to calculate the characteristic contact angle with water $\theta_v = 73^\circ$ using Eq. (2). We will compare the surface characteristics obtained for talc with the data in [99]: $q = 321 \text{ mJ}/\text{m}^2$, $\pi = 137 \text{ mJ}/\text{m}^2$, $\theta_v = 70.6^\circ$. While the π and θ_v values coincide with the data in Table 4, the specific heat of wetting $q = 195 \text{ mJ}/\text{m}^2$ that we obtained differs substantially from the value given in [99]. Since the temperature coefficient $d\theta/dT$ is close to zero for $\theta = 70.6^\circ$ (Table 1), the last term in Eq. (9) can be disregarded, and the correctness of the q value can be checked by means of Eq. (11). By substituting $\pi = 137 \text{ mJ}/\text{m}^2$ and $\theta_v = 70.6^\circ$ in this equation it was possible to obtain $q = 210 \text{ mJ}/\text{m}^2$, which is close to the value $q = 195 \text{ mJ}/\text{m}^2$ that we obtained (Table 4) but differs substantially from the value $q = 321 \text{ mJ}/\text{m}^2$.

The discrepancy between the values of π and q given in [99] is most likely due to the increased temperature for the vacuum treatment of the talc sample used to measure the heat of wetting. In [124] the $q(T)$ dependence was investigated for talc

TABLE 5. The Thermodynamic Characteristics of the Surface of Hydromica, Quartz, and the Basal Faces of the Talc Particles

Sorbent	σ_S , mJ/m ²	H_S , mJ/m ²	S_S , mJ/(m ² ·K)	σ_{SL} , mJ/m ²	H_{SL} , mJ/m ²	S_{SL} , mJ/(m ² ·K)
Hydromica	480	535	0.19	150	50	-0.34
Quartz	455	505	0.17	168	75	-0.32
Talc (the basal faces)	127	196	0.24	7.4	54	0.16

from the same deposit as in [99], and it was shown that a value of $q \approx 320$ mJ/m² is characteristic of a sample submitted to preliminary vacuum treatment at 250-260 °C. The step on the $q(T)$ relation at this temperature indicates the beginning of dehydroxylation of the mineral, which takes place vigorously at 400 °C, and as a result the value of q increases to 500 mJ/m². At the temperature (120 °C) that we used for vacuum treatment of the talc, which secures almost complete removal of the adsorbed water from the surface of the layer silicates but does not affect the constitutional water [112], the heat of wetting of the sample investigated in [99] is in the order of 220 mJ/m² [124], which is close to the data in Table 4 and, more importantly, almost coincides with the calculated value of q obtained according to Eq. (11) with the data from [99].

Talc has two types of surface – hydrophobic and hydrophilic. According to data in [125], the hydrophilic surface of talc amounts to 30-60% of its total surface. Electron-microscopic investigations [126] showed that the fraction of hydrophilic side faces in the investigated sample of talc amounted to 15% of its total surface. In the nature of the active centers (SiOH and MgOH groups) the side faces of the mica crystals are identical to the outer surface of magnesium silicate palygorskite. From the data in [99, 127] it is possible to determine its typical values $\pi = 257$ mJ/m² and $q = 495$ mJ/m², $q/\pi = 1.93$. We will use these values for the side faces of the talc particles. This makes it possible to determine the same characteristics for the basal hydrophobic surface of the mineral particles: $\pi = 107$ mJ/m² and $q = 142$ mJ/m², $q/\pi = 1.33$. By means of Eq. (9) we find that the contact angle of the basal faces of talc with water amounts to $\theta_v = 80^\circ$. The obtained value coincides with the data in [128, 129].

For the freshly revealed cleavage plane (the basal surface) in talc crystals the contact angle at the talc–water–air interface amounted to $\theta_a = 80^\circ$ - 90° [130]. In view of the fact that the difference $\theta_a - \theta_v$ in the region of large wetting angles is approximately 10° [69] these experimental data also confirm the results presented above.

Isomorphous substitutions are practically absent in the tetrahedral and octahedral networks of the talc structure. The surface oxygen atoms of the siloxane bonds do not therefore carry a negative charge as, for example, in micas, and as a result the basal surface of the talc crystals has clearly defined hydrophobicity. The equations of the Girifalco–Good theory [Eqs. (5) and (10) respectively] are then quite suitable for calculation of their surface free energy σ_S and surface enthalpy H_S . The value $\Phi = 0.74$ was used as interaction parameter. For graphite, which has a π value close to the basal faces of the talc particles (see Tables 2 and 4), the value $\Phi \approx 0.5$ deviates strongly from unity, reflecting the presence a small amount of active hydrophilic centers on the graphite surface. There are no such centers on the basal faces of the talc particles.

The obtained π , q , and θ_v values were also used during calculation of the thermodynamic surface characteristics of hydromica and quartz and their interfacial region at the boundary with water. The interfacial surface free energy σ_{SL} at the adsorbent–water boundary was calculated by means of Young’s equation, written in the following form:

$$\sigma_S = \sigma_{SL} + \pi + \sigma_{LV} \cos \theta. \quad (12)$$

The excess surface enthalpies of hydromica and quartz were obtained from the approximate Brunauer equation $\sigma_S = 0.9H_S$. The interfacial enthalpies of the investigated sorbents at their boundary with water were determined from the rigorous equation $H_{SL} = H_S - q$. The results are summarized in Table 5.

As follows from theory [1], the σ_S , H_S , and S_S values are positive. The S_{SL} value for the basal faces of talc particles is positive, indicating a disordered structure for the adsorbed water compared with liquid water. The negative value of S_{SL} for hydrophilic hydromica and quartz indicates directly that the structure of the water in the interfacial region is more ordered than for liquid water. This conclusion agrees well with the thermodynamic characteristics of water adsorbed by hydrophilic materials (e.g., see [38, 71]).

One important point must be emphasized. In the case of high-energy hydrophilic surfaces, for which the contact angle is close to zero, there must be a correlation between the surface pressure of the film of adsorbed water and the surface free energy. It follows from Tables 4 and 5 that $\pi/\sigma_S = 253/480 = 0.53$ for hydromica and $\pi/\sigma_S = 215/455 = 0.47$ for quartz. The average π/σ_S ratio for highly hydrophilic surfaces is 0.5.

The experimental determination of σ_S for high-energy surfaces presents greater difficulties [1], and it has in fact only been realized for a few dispersed materials. With the use of the empirical relation $\pi/\sigma_S \approx 0.5$ it is therefore possible to determine the surface free energy of many sorption-active materials. For example, for the external surface of palygorskite with $\pi = 257$ mJ/m² (see above) $\sigma_S \approx 515$ mJ/m², for Ca-kaolinite with $\pi \approx 240$ mJ/m² [68] $\sigma_S \approx 480$ mJ/m², and for hematite with $\pi \approx 140$ mJ/m² [120] $\sigma_S \approx 280$ mJ/m².

In conclusion we mention that important mutually compatible physicochemical characteristics (the surface pressure of an adsorbed film of water π , the specific heat of wetting q , and the contact angles θ for a series of oxides, silicates, and modified sorbents based on them) were presented in this review on the basis of a comparative analysis of a large amount of published and our own experimental data and successful application of the Gibbs–Helmholtz–Young equation. The total thermodynamic characteristics of the surface and the interfacial region at the boundary with water for hydrophilic and hydrophobic adsorbents were determined for the first time by means of these data. The important conclusion that the combined water close to the hydrophilic surfaces has a more ordered structure than liquid water and that water close to the hydrophobic surfaces has a less ordered structure was reached on the basis of interfacial entropy data. An empirical relationship linking the surface pressure of an adsorbed water film and the surface free energy for high-energy surfaces was proposed.

REFERENCES

1. A. I. Rusanov and V. A. Prokhorov, *Interfacial Tensiometry* [in Russian], Khimiya, St. Petersburg (1994).
2. V. B. Fainerman, D. Vollhardt, and G. Emrich, *J. Phys. Chem. B*, **105**, No. 19, 4324–4330 (2001).
3. R. Miller, A. V. Makievski, and V. B. Fainerman, *Surfactants: Chemistry, Interfacial Properties and Application*, V. B. Fainerman, D. Möbius, and R. Miller (eds.), Elsevier, Amsterdam (2001), pp. 287–400.
4. M. R. Maksimyuk, E. V. Aksenenko, V. V. Goncharuk, and V. Ya. Poberezhnyi, *Khim. Tekhnol. Vody*, **24**, No. 6, 516–525 (2002).
5. G. Para, E. Jarek, and P. Warszynski, *Colloids Surfaces A*, **261**, Nos. 1–3, 65–73 (2005).
6. V. N. Khabarov, A. I. Rusanov, and N. N. Kochurova, *Kolloid. Zh.*, **38**, No. 1, 120–125 (1976).
7. Yu. I. Tarasevich, *Khim. Tekhnol. Vody*, **11**, No. 3, 226–228 (1989).
8. M. V. Fedotova and V. N. Trostin, *Zh. Fiz. Khim.*, **79**, No. 9, 1602–1608 (2005).
9. B. D. Summ, *Zh. Fiz. Khim.*, **79**, No. 2, 199–212 (2005).
10. B. F. Ormont, *Introduction to Physical Chemistry and Crystal Chemistry of Semiconductors* [in Russian], Vysshaya Shkola, Moscow (1973).
11. J. V. Gibbs, *Thermodynamics. Statistical Mechanics* [in Russian], Nauka, Moscow (1982).
12. U. Danning, *Physics and Chemistry of the Solid State of Organic Compounds* [Russian translation], D. Fox, M. M. Leiba, and A. D. Weissberger (eds.), Mir, Moscow (1967), pp. 361–402.
13. A. Adamson, *Physical Chemistry of Surfaces* [Russian translation], Mir, Moscow (1979).
14. R. Shuttleworth, *Proc. Phys. Soc. A*, **63**, No. 365, 444–457 (1950).
15. E. Flad, *Gas–Solid Interface* [Russian translation], E. Flad (ed.), Mir, Moscow (1970), pp. 18–76.
16. S. Brunauer, *Pure Appl. Chem.*, **10**, No. 4, 293–307 (1965).
17. G. Benson and K. Yun, *Gas–Solid Interface* [Russian translation], E. Flad (ed.), Mir, Moscow (1970), pp. 172–229.

18. A. Ya. Gokhshtein, *Surface Tension of Solids and Adsorption* [in Russian], Nauka, Moscow (1976).
19. E. Papirer and H. Balard, *The Surface Properties of Silicas*, A. P. Legrand (ed.), John Wiley, New York (1998), pp. 315-364.
20. Yu. S. Lipatov, *Interphase Effects in Polymers* [in Russian], Naukova Dumka, Kiev (1980).
21. P. P. Pugachevich, É. M. Beglyarov, and I. A. Lavygin, *Surface Phenomena in Polymers* [in Russian], Khimiya, Leningrad (1982).
22. B. Janczuk and T. Bialopiotrowicz, *J. Colloid Interface Sci.*, **140**, No. 2, 362-372 (1990).
23. D. Li and A. W. Newmann, *J. Colloid Interface Sci.*, **148**, No. 1, 190-200 (1992).
24. C. Della Volpe, D. Maniglio, M. Brugnara, et al., *J. Colloid Interface Sci.*, **271**, No. 2, 434-453 (2004).
25. S. Siboni, C. Della Volpe, D. Maniglio, and M. Brugnara, *J. Colloid Interface Sci.*, **271**, No. 2, 454-472 (2004).
26. H. Tavana, N. C. C. Lam, K. Grundke, et al., *J. Colloid Interface Sci.*, **279**, No. 2, 493-502 (2004).
27. V. V. Yaminskii, E. A. Amelina, and E. I. Shchukin, *Surface Forces in Thin Films* [in Russian], B. V. Deryagin (ed.), Nauka, Moscow (1979), pp. 13-20.
28. E. D. Shchukin, I. V. Videnskii, E. A. Amelina, et al., *Kolloid. Zh.*, **60**, No. 5, 588-591 (1998).
29. B. V. Deryagin, N. F. Kromova, and V. P. Smilga, *Adhesion of Solids* [in Russian], Nauka, Moscow (1973).
30. J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, New York (1985).
31. E. A. Amelina, I. V. Videnskii, N. I. Ivanova, et al., *Kolloid. Zh.*, **63**, No. 5, 581-585 (2001).
32. J. N. Israelachvili and G. E. Adams, *J. Chem. Soc., Faraday Trans. I*, **74**, No. 4, 975-1001 (1978).
33. R. M. Pashley and J. N. Israelachvili, *Colloids Surfaces*, **2**, No. 1, 169-187 (1981).
34. J. N. Israelachvili and R. M. Pashley, *J. Colloid Interface Sci.*, **98**, No. 2, 500-514 (1984).
35. T. Young, *Phil. Trans. Roy. Soc. (London)*, **95**, 65-87 (1805).
36. P. M. Claesson, Ch. E. Blom, P. Herder, et al., *J. Colloid Interface Sci.*, **114**, No. 1, 234-242 (1986).
37. Yu. I. Tarasevich, *Ukr. Khim. Zh.*, **59**, No. 2, 150-157 (1993).
38. Yu. I. Tarasevich, I. G. Polyakova, and V. E. Polyakov, *Adsorp. Sci. Technol.*, **20**, No. 9, 927-935 (2002).
39. Yu. I. Tarasevich, G. V. Lantukh, A. I. Zhukova, and S. V. Bondarenko, *Teor. Éksp. Khim.*, **18**, No. 4, 470-476 (1982).
40. R. M. Pashley, P. M. McGuiggan, and B. W. Ninham, *Science*, **229**, No. 4718, 1088-1089 (1985).
41. G. F. Walker, *Clay Miner.*, **7**, No. 1, 129-143 (1967).
42. Yu. I. Tarasevich, S. V. Bondarenko, and A. I. Zhukova, *Kolloid. Zh.*, **42**, No. 6, 1128-1135 (1980).
43. L. A. Girifalco and R. J. Good, *J. Phys. Chem.*, **61**, No. 7, 904-909 (1957).
44. R. J. Good, L. A. Girifalco, and G. A. Kraus, *J. Phys. Chem.*, **62**, No. 11, 1418-1421 (1958).
45. R. J. Good and L. A. Girifalco, *J. Phys. Chem.*, **64**, No. 5, 561-565 (1960).
46. R. J. Good, *J. Colloid Interface Sci.*, **59**, No. 3, 398-419 (1977).
47. J. H. Hildebrand and R. L. Skott, *Solubility of Nonelectrolytes*, Reinhold Publ. Co., New York (1950).
48. I. R. Prigozhin, *Molecular Theory of Solutions* [in Russian], Metallurgiya, Moscow (1990).
49. Yu. I. Tarasevich, *Teor. Éksp. Khim.*, **42**, No. 2, 87-91 (2006).
50. R. J. Good and F. P. Baff, *Modern Capillarity Theory* [Russian translation], A. I. Rusanov and F. Ch. Gudrich (eds.), Khimiya, Leningrad (1980), pp. 62-85.
51. W. A. Zisman, *Adv. Chem. Ser.*, No. 43, 1-51 (1964).
52. B. D. Summ and Yu. V. Goryunov, *Physicochemical Principles of Wetting and Flow* [in Russian], Khimiya, Moscow (1976).
53. F. M. Fowkes, *Adv. Chem. Ser.*, No. 43, 99-111 (1964).
54. D. K. Owens and R. Wendt, *J. Appl. Polym. Sci.*, **13**, No. 8, 1741-1747 (1969).
55. J. Van Oss, R. J. Good, and M. K. Chaudhury, *Langmuir*, **4**, No. 4, 884-891 (1988).
56. Yu. Lipatov and A. Feinerman, *Adv. Colloid Interface Sci.*, **11**, No. 3, 195-293 (1979).
57. J. Kloubek, *Adv. Colloid Interface Sci.*, **38**, No. 1, 99-142 (1992).
58. J. K. Spelt, *Colloids Surfaces*, **43**, Nos. 3/4, 389-411 (1990).
59. S. Shalel-Levanon and A. Marmura, *J. Colloid Interface Sci.*, **262**, No. 2, 489-499 (2003).
60. C. Jouany and P. Chassin, *Colloids Surfaces*, **27**, Nos. 1-4, 289-303 (1987).
61. B. Janczuk, E. Chibowski, T. Bialopiotrowicz, et al., *Clays Clay Miner.*, **38**, No. 1, 53-56 (1990).

62. A. Ben-Naim, *Hydrophobic Interactions*, Plenum Press, New York, London (1980).
63. Yu. I. Tarasevich, *Structure and Chemistry of the Surface of Layer Silicates* [in Russian], Naukova Dumka, Kiev (1988).
64. M. E. Tadros, P. Hu, and A. W. Adamson, *J. Colloid Interface Sci.*, **49**, No. 2, 184-195 (1974).
65. P. Hu and A. W. Adamson, *J. Colloid Interface Sci.*, **59**, No. 3, 605-614 (1977).
66. J. W. Whalen and W. H. Wade, *J. Colloid Interface Sci.*, **24**, No. 3, 372-378 (1967).
67. D. H. Bangham and R. I. Razouk, *Trans. Faraday Soc.*, **33**, No. 11, 1459-1472 (1937).
68. Yu. I. Tarasevich, *Zh. Fiz. Khim.*, **64**, No. 9, 2452-2459 (1990).
69. J. W. Whalen and K. Y. Lai, *J. Colloid Interface Sci.*, **59**, No. 3, 483-489 (1977).
70. H. Schonhorn, *Nature*, **210**, No. 5039, 896-897 (1966).
71. Yu. I. Tarasevich, *Teor. Éksp. Khim.*, **29**, No. 2, 100-115 (1993).
72. K. G. Sabbatovskii, V. Dutschk, M. Nitschke, et al., *Kolloid. Zh.*, **66**, No. 2, 239-247 (2004).
73. E. Lindner and E. Arias, *Langmuir*, **8**, No. 4, 1195-1198 (1992).
74. L. Holysz, K. Terpilowski, and E. Chibowski, *Theoretical and Experimental Studies of Interfacial Phenomena and their Technological Applications: IX Polish-Ukrainian Symp. (Poland, Wolka Milanowska, Sandomierz, Sept. 5-9, 2005)*, Wydawn. Uniw. M.-Curie Sklodowskiej, Lublin (2005), pp. 62-64.
75. E. Chibowski, *Adv. Colloid Interface Sci.*, **103**, 149-172 (2003).
76. A. A. Pashchenko, M. G. Voronkov, L. A. Mikhaïlenko, et al., *Hydrophobization* [in Russian], Naukova Dumka, Kiev (1973).
77. B. V. Deryagin, *Dokl. Akad. Nauk SSSR*, **51**, No. 5, 357-360 (1946).
78. V. P. Elyutin, V. I. Kostikov, and A. V. Kharitonov, *Dokl. Akad. Nauk SSSR*, **182**, No. 2, 376-377 (1968).
79. J. Abrahamson, *Carbon*, **11**, No. 4, 337-362 (1973).
80. A. C. Zettlemoyer, *J. Colloid Interface Sci.*, **28**, No. 3/4, 343-369 (1968).
81. G. Kraus, *J. Phys. Chem.*, **59**, No. 4, 343-345 (1955).
82. Tu. I. Tarasevich, *Kolloid. Zh.*, **54**, No. 4, 191-193 (1992).
83. W. D. Harkins, *The Physical Chemistry of Surface Films*, Reinhold Publ. Co., New York (1952).
84. V. V. Turov and R. Lebeda, *Chem. Phys. Carbon*, **27**, 67-124 (2000).
85. I. Kalnin and Kh. Yager, *Carbon Fibers and Carbon Composites* [Russian translation], F. Fitzer (ed.), Mir, Moscow (1988), pp. 83-102.
86. J. B. Donnet, M. Brendle, T. L. Dhami, and O. P. Bahl, *Carbon*, **24**, No. 6, 757-770 (1986).
87. Q. Zhao, Y. Liu, and E. W. Abel, *J. Colloid Interface Sci.*, **280**, No. 1, 174-183 (2004).
88. H. Harttig and K. J. Huttinger, *J. Colloid Interface Sci.*, **78**, No. 2, 295-303 (1980).
89. A. V. Rao, M. M. Kulkarni, and T. S. Amalnerkar, *J. Non-Cryst. Solids*, **330**, 187-195 (2003).
90. I. B. Slinyakova and T. I. Denisova, *Organosilicon Adsorbents: Production, Properties, Application* [in Russian], Naukova Dumka, Kiev (1988).
91. Yu. I. Tarasevich, *Kolloid. Zh.*, **53**, No. 6, 1111-1113 (1991).
92. Yu. I. Tarasevich, V. E. Polyakov, A. A. Serdan, and G. V. Lisichkin, *Kolloid. Zh.*, **67**, No. 5, 702-708 (2005).
93. H. H. G. Jellinek, *J. Colloid Sci.*, **20**, No. 2, 801 (1965).
94. A. Yu. Fadeev, O. A. Soboleva, and B. D. Summ, *Kolloid. Zh.*, **59**, No. 2, 243-247 (1997).
95. Yu. I. Tarasevich, S. V. Bondarenko, and A. I. Zhukova, *Teor. Éksp. Khim.*, **42**, No. 2, 125-129 (2006).
96. A. Y. Fadeev and T. J. McCarthy, *Langmuir*, **16**, No. 18, 7268-7274 (2000).
97. H. P. Boehm, *Carbon*, **32**, No. 5, 759-769 (1994).
98. Yu. I. Tarasevich, S. V. Bondarenko, and A. I. Zhukova, *Adsorption*, **11**, Nos. 3/4, 385-391 (2005).
99. J. M. Douillard, J. Zajac, H. Malandrini, and F. Clauss, *J. Colloid Interface Sci.*, **255**, No. 2, 341-351 (2002).
100. Yu. G. Frolov, *Course of Colloid Chemistry* [in Russian], Khimiya, Moscow (1989).
101. Ya. E. Geguzin and N. N. Ovcharenko, *Usp. Fiz. Nauk*, **86**, No. 2, 283-328 (1962).
102. I. W. Obreimoff, *Proc. Roy. Soc. A*, **127**, No. 805, 290-297 (1930).
103. I. V. Obreimov and E. S. Trekhov, *Investigations in Experimental Theoretical Physics* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1959), pp. 159-174.

104. M. S. Metsik, *Physics of Cleavage of Micas* [in Russian], Vost.-Sib. Kn. Izd., Irkutsk (1967).
105. R. F. Giese, *Nature*, **248**, No. 5449, 580-581 (1974).
106. A. I. Bailey and S. M. Kay, *Proc. Roy. Soc. A*, **301**, No. 1464, 47-56 (1967).
107. Yu. I. Tarasevich, *Kolloid. Zh.*, **54**, No. 4, 186-190 (1992).
108. S. Brunauer, *J. Colloid Interface Sci.*, **59**, No. 3, 433-437 (1977).
109. C. J. Van Oss, R. F. Giese, Z. Li, et al., *J. Adhes. Sci. Technol.*, **6**, No. 4, 413-418 (1992).
110. B. Janczuk, E. Chibowski, M. Hainos, et al., *Clays Clay Miner.*, **37**, No. 1, 269-272 (1989).
111. E. Chibowski and P. Staszczuk, *Clays Clay Miner.*, **36**, No. 5, 455-461 (1967).
112. Yu. I. Tarasevich and F. D. Ovcharenko, *Adsorption on Clay* [in Russian], Naukova Dumka, Kiev (1975).
113. J. Schultz, K. Tsutsumi, and J.-B. Donnet, *J. Colloid Interface Sci.*, **59**, No. 2, 277-282 (1977).
114. V. Médout-Marère, A. El Ghzaoui, C. Charnay, et al., *J. Colloid Interface Sci.*, **223**, No. 1, 205-214 (2000).
115. V. Médout-Marère, S. Partyka, and R. Dutarte, *J. Colloid Interface Sci.*, **262**, No. 2, 309-320 (2003).
116. W. F. Brace and J. B. Walsh, *Amer. Miner.*, **47**, Nos. 9/10, 1111-1122 (1962).
117. S. Brunauer, D. L. Kantro, and C. H. Weise, *Can. J. Chem.*, **34**, No. 10, 1483-1495 (1956).
118. Yu. I. Tarasevich, *Ukr. Khim. Zh.*, **51**, No. 2, 133-141 (1985).
119. M. M. Egorov and V. F. Kiselev, *Zh. Fiz. Khim.*, **36**, No. 2, 318-324 (1962).
120. Yu. I. Tarasevich, *Ukr. Khim. Zh.*, **59**, No. 3, 265-269 (1993).
121. J. W. Whalen, *J. Phys. Chem.*, **65**, No. 10, 1676-1681 (1961).
122. H. Malandrini, R. Sarraf, B. Faucompre, et al., *Langmuir*, **13**, No. 5, 1337-1341 (1997).
123. P. Staszczuk, *Chromatographia*, **20**, No. 12, 724-728 (1985).
124. L. Michot, J. Yvon, J. M. Cases, et al., *C. r. Acad. sci. Ser. II*, **310**, No. 8, 1063-1068 (1990).
125. C. Charnay, S. Lagerge, and S. Partyka, *J. Colloid Interface Sci.*, **233**, No. 2, 250-258 (2001).
126. S. Okuda, K. Inoue, and W. O. Williamson, *Proc. of Intern. Clay Conf. (Tokyo, Sept. 1969)*, Israel Univ. Press, Jerusalem (1969), Vol. 1, pp. 31-41.
127. J. J. Chessick and A. C. Zettlemoyer, *J. Phys. Chem.*, **60**, No. 9, 1181-1184 (1956).
128. L. Michot, F. Villieras, M. Francois, et al., *Langmuir*, **10**, No. 10, 3765-3773 (1994).
129. H. Malandrini, F. Clauss, S. Partyka, and J. M. Douillard, *J. Colloid Interface Sci.*, **194**, No. 1, 183-193 (1997).
130. G. S. Strel'tsyn, *Kolloid. Zh.*, **30**, No. 4, 592-595 (1968).