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Review

# Physicochemical properties of liquid–solid interfaces by means of controlled rate thermal analysis

Piotr Staszczuk

*Department of Physical Chemistry, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20031 Lublin, Poland*

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## Abstract

This paper sums up the possible application of controlled rate thermal analysis methods to study liquid–solid interactions and the physicochemical properties of liquid films and solid surfaces, using mainly the programmed thermodesorption of liquid from the sample. The results prove the applicability of this approach in the determination of adsorption value, thermodynamic functions, properties of adsorbed layers and the heterogeneity of porous materials. One principal idea of these studies was to register the effects taking place in processes opposite to adsorption, i.e. in the controlled rate thermodesorption of liquids from solid surfaces. The method utilized the differential time and temperature weight-loss (DTG) dependences of the thermogravimetric (TGA) curves as well as the differential scanning calorimetry (DSC) curves obtained during cooling and heating at subambient and elevated temperatures. It can be concluded that thermal analysis is a simple, useful and effective method, besides its classical applications, in characterizing liquid–solid systems. The author's most important results have been evaluated and published, or submitted for publication, in this and other scientific journals over the last past decade.

*Keywords*: CRTA; DTG; Film; Stability; Surface; TGA

## 1. Introduction

Thermal analysis (TA) is used to determine changes in the physicochemical properties of materials and liquids as a function of temperature [1–5]. The recent past has seen major developments in this analytical method and its numerous and

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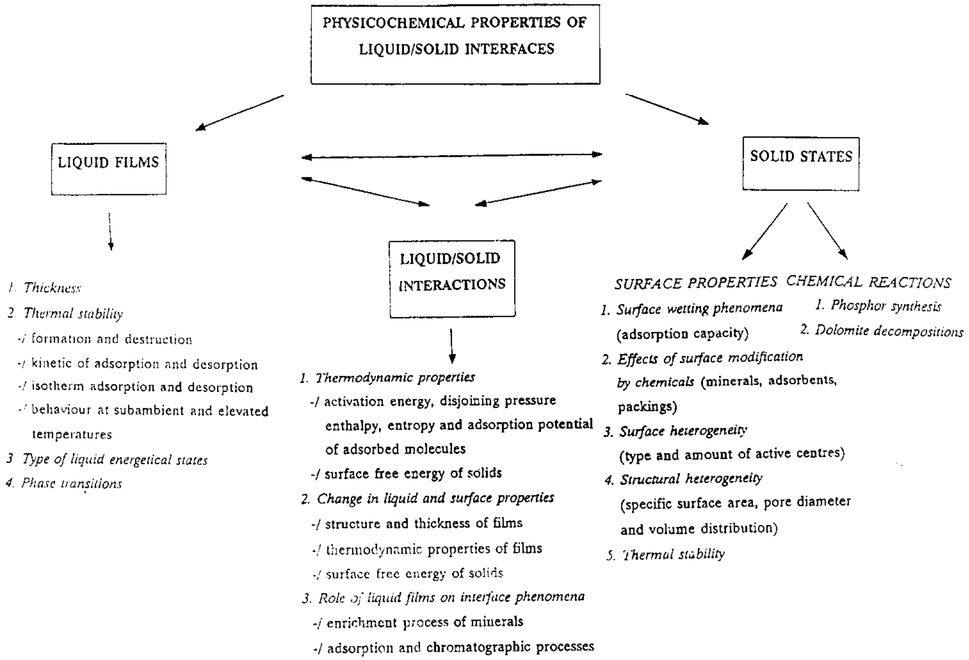
novel applications in science and technology [6–15]. Thus, TA is often used to characterize properties of solids (e.g. the identity, content and decomposition behavior of compounds, minerals, biological substances and pharmaceutical products) [1,2,3,5]. Recently, high-resolution thermogravimetric analysis (HR TGA) and differential scanning calorimetry (DSC) have been applied in calculating a simple model of the energetic heterogeneity and kinetic parameters [16,17], and various TA functions concerning heterogeneous processes have been reconsidered from a fractal viewpoint [18].

However, TA methods have rarely been used to study liquid–solid interfaces (e.g. adsorption capacity or porous structure) [19]. The combined TA "dynamic" method was employed to determine adsorption isotherms [20]. A derivatograph was also used to determine the thermal stability of industrial adsorbents and cements [21], as well as in studies of the kinetics of structural relaxation of amorphous silica gel [22,23], a number of hydroxyl groups [24,25], and to investigate the content and type of water in chemical compounds. The method was also adopted to study the dehydration processes of chemical compounds [26–30]. From the data of water thermodesorption from zeolites [31–33], the kinetics of this process were studied under isothermal and nonisothermal conditions, and can be presented as a first-order reaction. The values of water molecule activation energy and its distribution on the surface of the studied zeolites were calculated. Data from temperature-programmed desorption were successfully used in the calculation of surface site energy distributions [34].

Thermal analysis carried out under quasi-isothermal conditions has been widely applied in studies of chemical compound distribution and of the kinetics and mechanism of chemical reactions [35–38]. The years 1960–1965 were especially important for the development of modern controlled rate thermal analysis [39,40]. During that time, J. and F. Paulik and Rouquerol independently formulated the idea of automating the ultra-slow heating procedure in order to ensure, if possible, quasi-equilibrium conditions and to increase the resolution of thermal analysis. The interest in this type of study arises from features of the operation and course of the heating process as well as the transformation of the sample in the derivatograph crucible. Compared with studies carried out under dynamic conditions, quasi-isothermal methods have some advantages, among which are a wider range of application and much greater selectivity. The method is more reliable in investigations of transformations of "overlapping" processes. Using the quasi-isothermal method it is possible to determine, for examples, the quantity and temperature of the process of separation of water of crystallization separation from the compound under study, as well as its mechanism. This problem has been discussed in ref. [41] during the investigation of water thermodesorption from zeolite surfaces and in a review paper [42].

Attempts have therefore been made to work out the experimental basis and then the underlying theory of a quick and simple method for characterizing liquid–solid interactions and the properties of superficially heterogeneous solids and adsorbed films based on experimental data obtained from the process of programmed liquid thermodesorption from solid surfaces using computer calculations. Studies on the application of controlled thermal analysis in investigations of physicochemical properties of liquid–solid systems (character of adsorbent–adsorbate interactions, properties of adsorption layers and heterogeneity of solid surfaces) were begun by author of this paper 15 years ago. One major idea of these studies, compared with traditional methods (e.g. McBain balances, sorption balances and adsorption gas chromatography to measure parameters accompanying the adsorption process) was to use and register the effects taking place in the processes opposed to adsorption, that is, in the programmable thermodesorption of liquids from solid surfaces.

New problems and possibilities of application of TA techniques in a more comprehensive way appeared during the studies (Scheme 1). The papers quoted here present calculations of values of such thermodynamic functions as surface free energy and its components, adsorption film pressure and adsorption layer thickness, and also studies of the thermal stability of both adsorption layers and solid samples obtained by the programmable thermodesorption of liquids from solid surfaces. The latest papers describe the possibilities of application of TGA and DSC in characterizing porosity and number of hydroxyl groups on the surface of the studied samples, as well as energetic effects accompanying phase and structural changes of the adsorption film. The above mentioned parameters obtained by the use of TA were correlated with the corresponding measurements, such as those made by using McBain balances, porosimetry, chromatography and other adsorption techniques, and good agreement was found. The TA method was also used in studies of chemical reactions in the solid phase. Furthermore, studies on the synthesis of new halophosphates and the decomposition of dolomites were carried out. These studies resulted in new measurement techniques and some unique experimental results.



Scheme 1. Applications of controlled thermal analysis in the study of liquid–solid interfaces.

Measurements of the extent of adsorption of liquid from a gaseous phase, as well as programmed thermodesorption of liquid under dynamic and quasi-isothermal conditions from the surface of the studied solids, were made by means of a Q-1500 D derivatograph (MOM, Hungary), a model TGA 2950 thermogravimetric analyser equipped with an open pan and capable of maintaining quasi-isothermal conditions, and a model DSC 2910 differential scanning calorimeter equipped with a standard DSC cell and with subambient accessories (TA Instruments, Inc., New Castle, DE, USA).

The studies were carried out on solid surfaces with various heterogeneous properties: (i) pure materials such as minerals (quartz, coal, marble, barite) and porous adsorbents (aluminum oxide, silica gel, active carbon), (ii) materials modified by different chemicals (e.g. minerals covered with collectors), and (iii) other materials, e.g. latexes (polymers covered by ions) and "smart" surfaces (zeolites, or silica gel covered by proteins). The material under study was exposed to the adsorptive substance (water, n-alcohol, n-alkane, benzene or toluene) by different methods: (i) immersing the material in the pure liquid, (ii) exposing it to vapor in a vacuum desiccator (where $p/p_0 = 1$), and (iii) exposing it to water vapor in air. Detailed descriptions of the apparatus, methods and sample preparations are given in other papers [43-67,71-81]. Here the best results obtained in this field are presented.

## 2. Measurements of liquid adsorption and desorption from a gaseous phase

A modified derivatograph was used in adsorption and calorimetric studies at constant temperature. The results of measurements of adsorption and desorption of water from the gas phase and the heat of the processes on a silica gel surface are given in refs. [47-50]. Two papers [47,50] present a description of a modified derivatogaph of Q-1500 D type which enables measurement of sample weight change at constant temperature. Changes in sample weight take place as a result of adsorption and desorption processes of the vapor of a liquid (e.g. water) flowing in an inert gas (e.g. nitrogen) through a measuring chamber at constant temperature. From the obtained experimental data (Fig. 1), the water adsorption and desorption isotherms on silica gel were determined [48]. As follows from studies after the desorption process using pure dry nitrogen at 20°C, there remains the so-called vicinal water, the removal of which requires heating of the sample to 200°C.

The method of calculating the heat of water adsorption and immersion on silica gel from the DTA curve obtained by using a modified derivatograph is presented in ref. [49]. Fig. 2 shows the dependence of the calculated heat of adsorption on the value of water adsorption on silica gel, from which it follows that the greatest amount of heat is evolved during the stage of forming the first adsorption layers on the surface.

The free surface energy and its polar and dispersion components for silica gel with a chemically bonded $C_{18}$ phase for use in HPLC were calculated from derivatographic measurements of the adsorption of n-octane and water [51,52]. From these studies, correlations between the surface energy of the silica gel sample and the extent of coverage by the chemically bonded phase and also the surface concentration of silanol groups were established (Fig. 3). Adsorption measurements

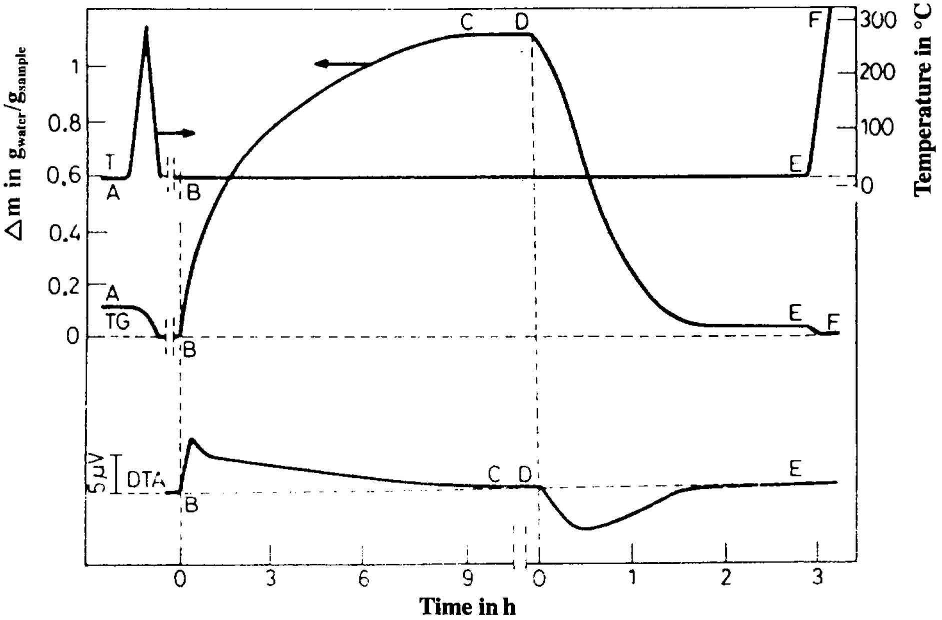


Fig. 1. The TA, TG and DTA curves corresponding to adsorption and desorption of water vapor onto and from silica gel at 20°C [47]. TA curve: peak AB, sample heating to 300°C and cooling to 20°C; sector BE, constant temperature (20°C) during measurement; sector EF, sample heating to 300°C after the desorption process. TG curve: sector AB, evaporation of hygroscopic and vicinal water; BC, adsorption of water; CD, plateau; DE, desorption of water; EF, thermal desorption of water. DTA curve: sector BC corresponds to the heat of water adsorption on silica gel; CD, plateau; sector DE, the heat of desorption of water from the silica gel surface.

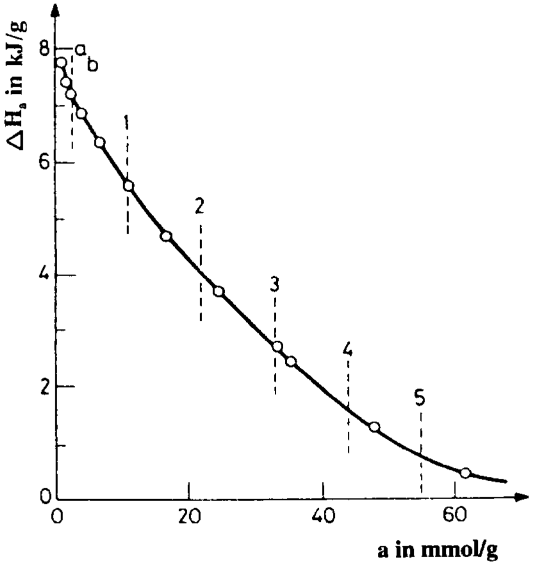


Fig. 2. Change of heat of adsorption in relation to the amount of water adsorbed on silica gel. Statistical monolayers of adsorbed water are denoted on the curve ($a_b$, amount of bonded water) [49].

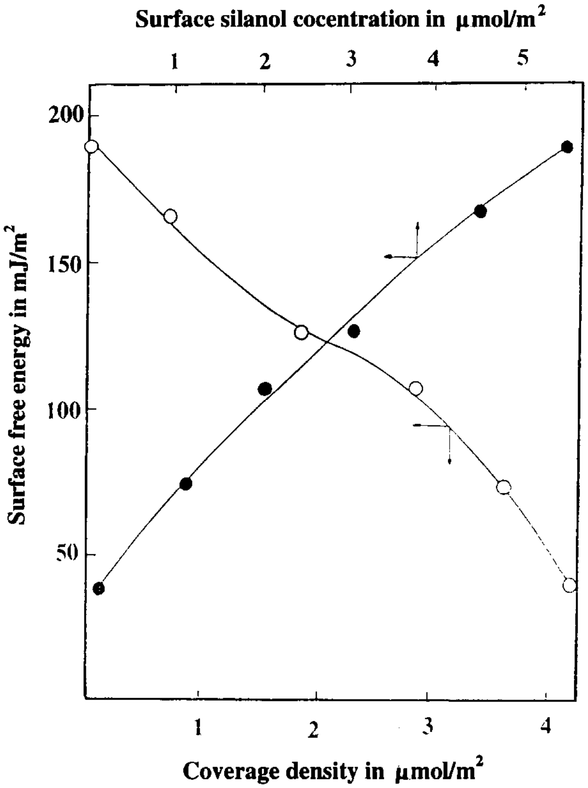


Fig. 3. Relationship of total surface free energy of packings vs. coverage density and surface silanol concentration [51].

were carried out using a modified device, and surface free energy and its components for various solids, such as halophosphates [53], carbon [54], marble, barite [55,56] and aluminum oxides [57], were calculated.

The modified derivatograph enables the effective use of differential thermal analysis in adsorption and calorimetric studies as well as classical measurements and the determination of the energetic and structural heterogeneity of the studied surface on the basis of the isotherms obtained.

## 3. Measurements using a classical "dynamic" program

A "dynamic" program, consisting in heating a measuring chamber at a constant rate, was used to study the synthesis and phase transitions of luminophores in the solid phase [58], the decomposition of dolomite [59,60] and liquid thermodesorption from solid surfaces.

The experimental studies revealed at least two or three peaks or points of inflection on the DTA and DTG curves of water thermodesorption from the surfaces of the studied samples (Fig. 4) [43,44,57]. These features result from the difference in binding energy of water molecules in adsorption layers and at the

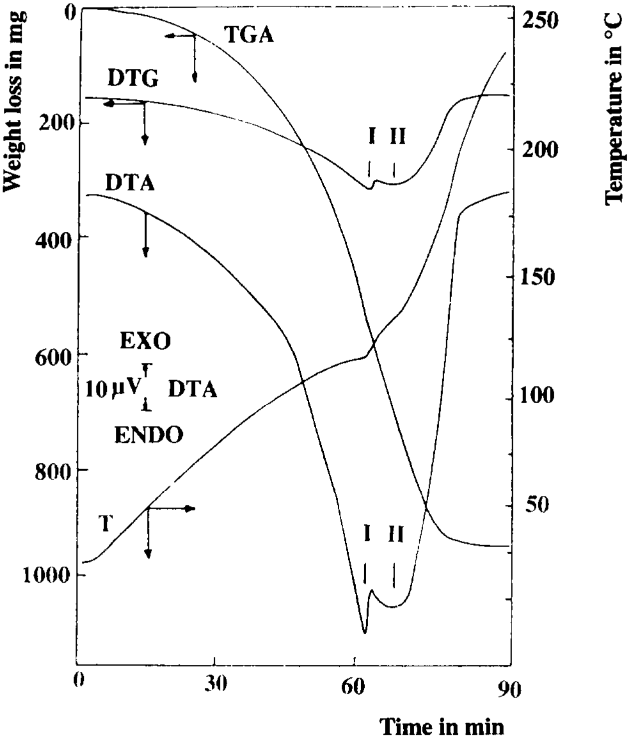


Fig. 4. Dynamic thermal curves of water thermodesorption from aluminum oxide [57].

studied surfaces. On the basis of the studies, it appears that the mechanism of thermodesorption from solid surfaces can be divided into the following stages: evaporation of bulk water added in excess to the studied sample, desorption of intergranular and capillary water and, finally, desorption of water both included in pores and adsorbed on the solid surface.

Reference [45] includes studies on water thermodesorption under dynamic conditions from a silica gel surface (Fig. 5). From the obtained experimental results, the activation energy, heat of dehydration, surface free energy and water film pressure were calculated on the basis of a modified Gibbs–Duhem equation

$$\pi_n = -\gamma_{T_n} + \Delta T_n \Delta S_m \tag{1}$$

and

$$\gamma_{T_n} = -RT_n \int_{p_n}^{p} a^s \mathrm{d}(\ln p_n) \tag{2}$$

where $a^s$ is the amount of desorbed water, $S_m$ is the entropy change corresponding to the transfer of water from liquid phase to vapor, $\gamma_{Tn}$ is the interfacial tension in the silica gel–water system corresponding to film pressure $\pi_n$ on the surface at temperature $T_n$ and water vapor pressure $p_n$, $p_0$ is the saturated water vapor pressure and $R$ is the gas constant.

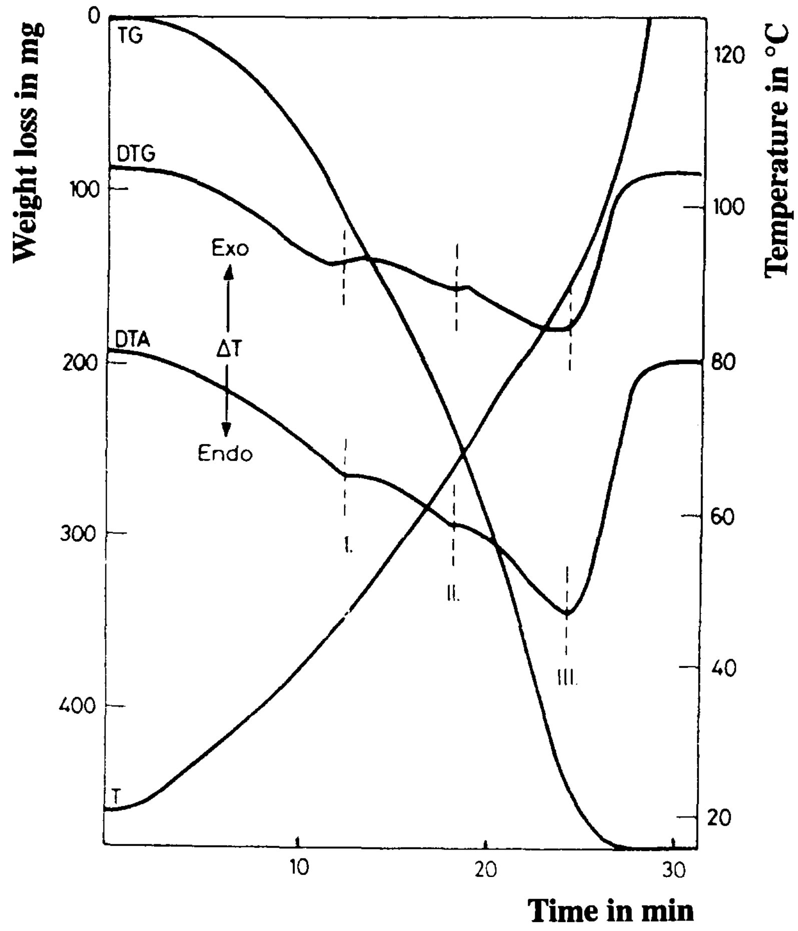


Fig. 5. Dynamic thermal curves of water thermodesorption from silica gel [45].

Correlations of changes in water film pressure and the values of the work of spreading, immersion and adhesion wetting are presented in Fig. 6. The value of surface free energy on the studied silica gel was calculated from Fowkes's equations [45].

Using this method, the properties of water films on marble and barite surfaces covered with tetradecylammonium chloride (TDAHCl) were studied before and after the process of enrichment by the flotation method [55,56]. The influence of the amount of adsorbed TDAHCl on the water film thickness, activation energy, enthalpy, entropy and vicinal water molecules was determined (Fig. 7). From the obtained data, possible structures of water, their changes depending on the amount of TDAHCl earlier added to the studied surface, as well as influences on the mechanism and effectiveness of the enriching mineral process were discussed.

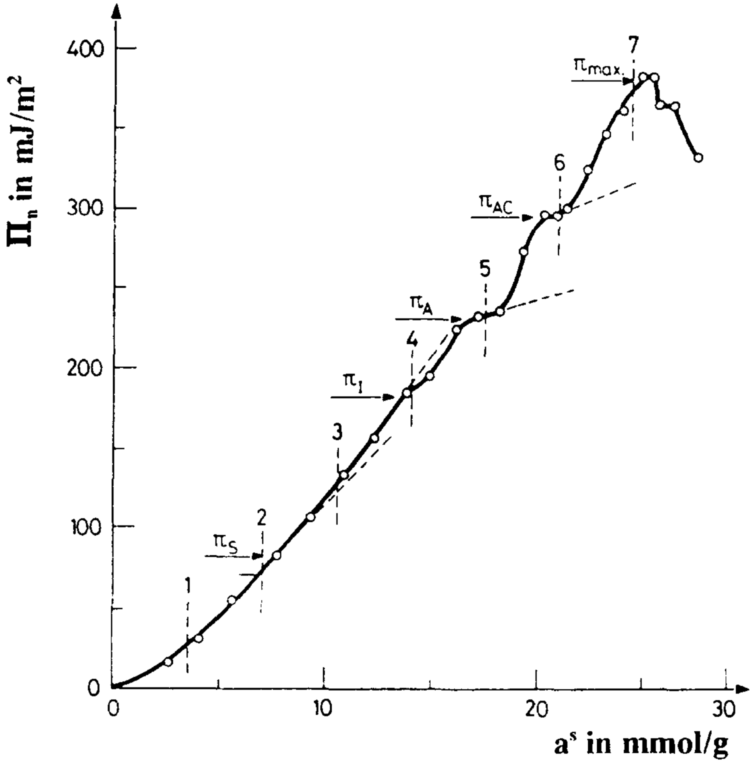


Fig. 6. Dependence of water film pressure on the amount of desorbed water [45].

## 4. Measurements of programmed liquid thermodesorption under quasi-isothermal and high-resolution conditions

As mentioned above, literature reports on the application of this method in physicochemical studies of liquid–solid systems are scarce [38]. Fig. 8 depicts a typical thermal decomposition carried out under quasi-isothermal conditions on hydrated copper sulfate. It follows from this figure that the type and amount of water of crystallization evolved from the sample depend on the transformation temperature [61,62].

Based on earlier studies on programmed thermodesorption under quasi-isothermal conditions [45,55,56,62–67] it was stated that the properties of water present on the surface of various solids changed in stepwise fashion with the distance from the surface, but not exponentially (monotonically) as suggested in the literature [68–70]. From the obtained curves of $m = f(T)$, where $m$ is the mass loss and $T$ is temperature, the thickness of the surface water film with changed properties as well as a static number of water monolayers of vicinal water on silica gel [45], aluminum oxide [57] and active carbon [65] were calculated. This characteristic "stepwise" thermodesorption process of water and other liquids from solid surfaces was explained in the papers cited above by a change of the wetting process mechanism and a change of water

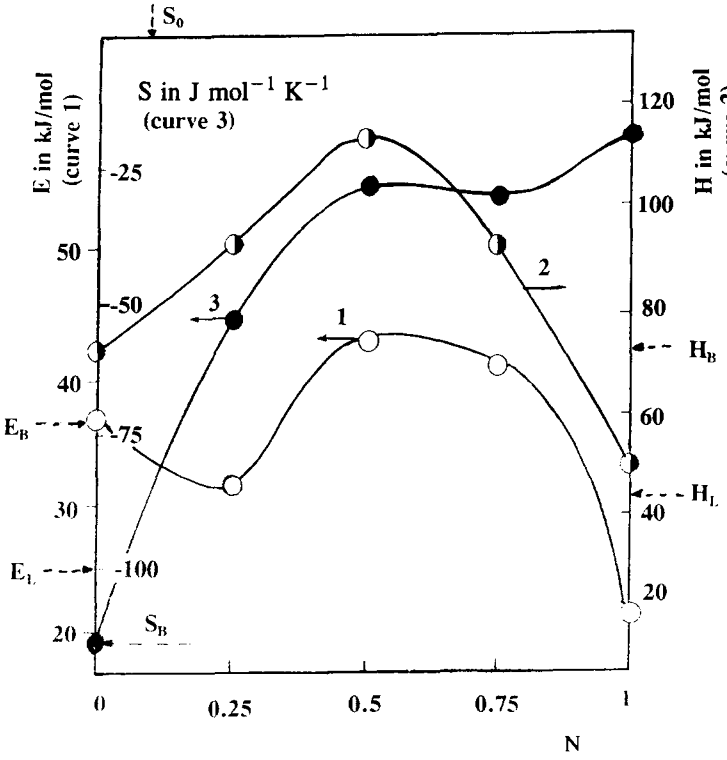


Fig. 7. Activation energy $E$ (curve 1), enthalpy $H$ (curve 2) and entropy $S$ (curve 3) of water evaporation from the surface as a function of the statistical TDAHCl monolayer N coverage deposited on barite (subscript B, bonded water; subscript L, volume water) [55,56].

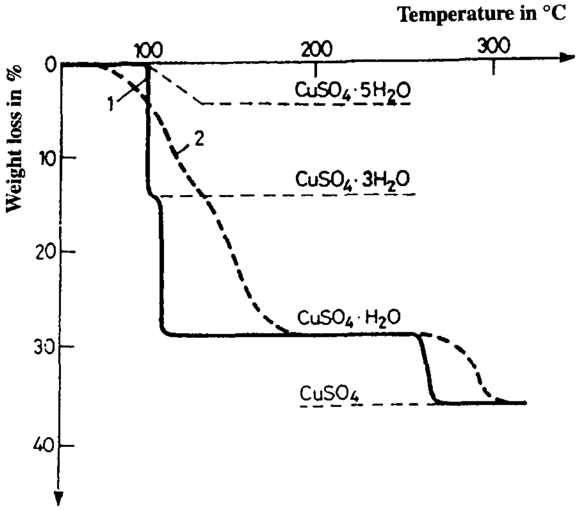


Fig. 8. Thermal decomposition of $CuSO_4 \cdot 5H_2O$ under quasi-isothermal conditions (1, "quasi-isothermal" curve; 2, "dynamic" classical curve) [62].

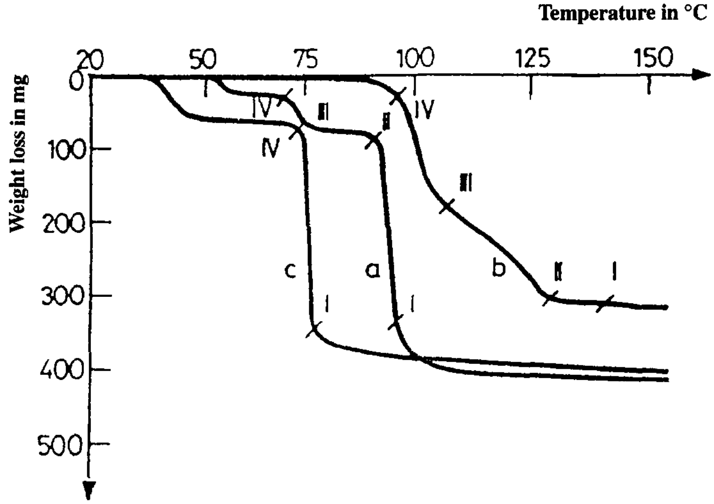


Fig. 9. Thermodesorption under quasi-isothermal conditions of propanol (curve a), octane (curve b) and benzene (curve c) from active carbon surfaces [71].

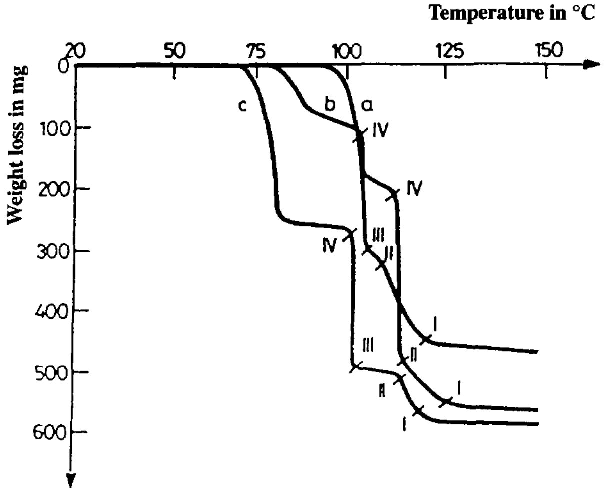


Fig. 10. Water thermodesorption under quasi-isothermal conditions from aluminum oxide (curve a), silica gel (curve b) and active carbon (curve c) surfaces [71].

structure due to interactions of surfaces, capillary forces, and macro-, meso- and micropores of the solid (Figs. 9 and 10).

The results of studies on the thermodesorption of water from solid surfaces presented in earlier papers [55–57,62–66] show that there are at least three inflection points on each curve of liquid thermodesorption from the surface of the studied samples, much as in the dynamic method. This is the reason for the difference in energy of liquid molecule binding in adsorption layers and with the sample surface. The thermodesorption process of water from the surface of samples of hydrophobic character (coal, sulfur) or minerals of crystalline and non-porous character (quartz, marble, barite) possessing small specific surface areas can be divided into two stages: evaporation of bulk water added to the sample in excess and desorption of intergranular and capillary water with a small amount of water adsorbed in micropores and on the surface of the studied solid, i.e. vicinal water.

With the increase of porosity, and resulting from the specific surface area of such adsorbents as aluminum oxide, silica gel and active carbon, the number of thermodesorption stages increases as shown on the curves presented in Figs. 9 and 10 and the stages become more distinct. In the case of active carbon, there are various active centers present on the surface such as macro-, meso-, micro- and even submicropores, which determine the properties of both the surface and the adsorbed liquid layers [65]. The greatest influence of the surface was observed during studies of the water–active carbon system (Fig. 10, curve c; a very distinct "stepwise" type of thermodesorption) because of changes of water film properties (mainly structural) [65]. This effect results from the dipole structure of water and the influence of various types of surface pores and active centers of different energies (heterogeneous character of the active carbon surface) on its molecules. This effect is smaller in the case of propanol (Fig. 9, curve a), octane (curve b) and benzene (curve c).

In this case the mechanism of the thermodesorption process can be interpreted as follows. The first stage (Figs. 9 and 10) is the evaporation of bulk water added to the sample in excess (up to inflection IV). The next stages of evaporation (between inflections IV and I) involve the desorption of water included in capillaries as well as in macro-, meso- and micropores of the studied sample. The last stage (from inflection I to the end of the process) is the thermodesorption of water closely bonded in submicropores and adsorbed on the sample surface. This is the most interesting stage of the process from a cognitive point of view, as it provides information about the character of the studied surface (among others, the type of interactions and the distribution of adsorption potential). Removal of this water takes place at the highest temperature of the process (generally above 120°C), as it requires much energy. This water layer possesses a modified ice-like structure. Each water molecule in a structure of this type is bound to its neighbors by four hydrogen bonds, and the value of hydrogen bond energy between the molecules is 40–45 kJ $\mathrm{mol}^{-1}$ [68]. The thickness of the layer of bound water is not well known because of changes in its structure which take place in $10^{-12}$ s [69,70] and because of the dispersive and non-dispersive interaction of water with surface active centers of different energies. It should be noted that the values for the amount of water adsorption from the gaseous phase at 20°C are comparable with the amount of water desorbed corresponding to inflection II in Figs. 9 and 10, despite being obtained by different methods and under different measurement conditions [55,56,62–66]. This concurrence probably results from the range of interaction of surface forces on the water molecule and the area of ice-like structure formation in the liquid films close to the surface. This phenomenon was observed and discussed earlier in other systems studied [55,56].

Reference [65] showed the dependence between the thickness of the water film on the surface possessing changed properties and the volume of active carbon micro-

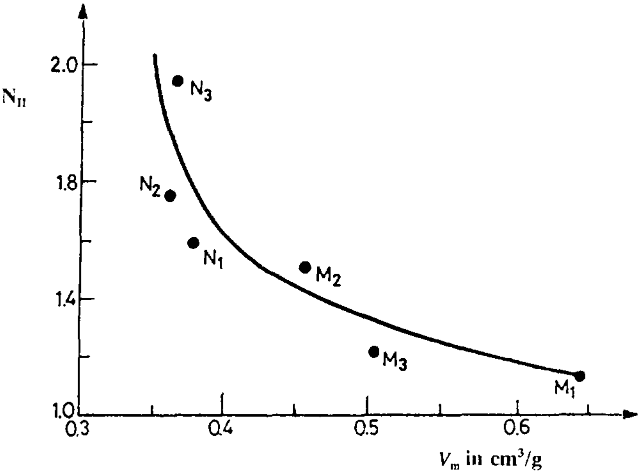


Fig. 11. The number of statistical monolayers of desorbed water corresponding to inflection point II on Q-TG curves as a function of the micropore volume of Merck (M) and Norit (N) active carbons [65].

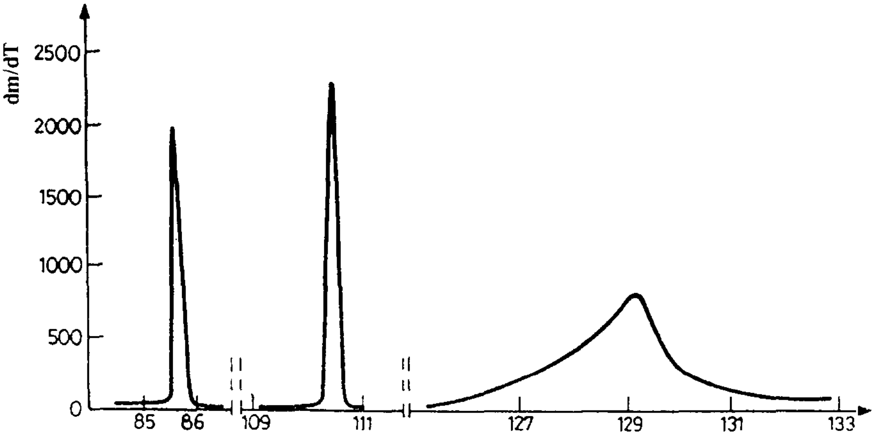


Fig. 12. Derivative of mass loss of benzene from active carbon surface with respect to temperature [62].

pores (Fig. 11). The $V_m$ parameter characterizes the porous structure of the carbons studied. Activated carbons prepared from Norit carbon possess lower values of $V_m$ in comparison with modified Merck carbons. The carbons $N_1$, $N_2$ and $N_3$ contain micropores with slightly smaller diameters than carbons $M_1$, $M_2$ and $M_3$. This is the reason for the changes in water film properties following with effect of the overlap of adsorption forces generated by the opposite walls of the slit-like micropores.

Because of the high resolution and selectivity of the "step", resulting mainly from large specific surface area and sample porosity, measurements of programmed thermodesorption of benzene under quasi-isothermal conditions from active carbon samples were used in further calculations of, among others, adsorption potential distribution [66,67]. Fig. 12 gives the calculated values $dm/dT = f(T)$ taken from the Q-TG curve obtained for the benzene–active carbon system [62]. The dependence is due to the distribution function of the activation energy of desorption. Such functions are characterized by the heterogeneity of the adsorbent resulting from the so-called structural heterogeneity of the micropores, as well as heterogeneity related to the existence of various adsorption centers, i.e. surface heterogeneity. Based on the data for liquid thermodesorption from solid surfaces under quasi-isothermal conditions ($m = f(T)$ dependences), the value of the adsorption potential $A$, which means the change of molar free energy related to the change of liquid vapor pressure $p_n/p_0$ at a given packing of the surface layer, was calculated from the equation

$$A = RT_n \ln(p_n/p_0) \tag{3}$$

where $p_n$ is the equilibrium pressure of the adsorbate, $p_0$ is the saturated vapor pressure of the adsorbate at temperature $T_n$ and $R$ is the gas constant.

Subsequently, the dependence $da/dA = f(A)$, where $a$ is the liquid desorption value in mmol $g^{-1}$, for the systems of benzene–active carbon [62,66,67,71], benzene–silica gel [73] and water–latex [74] was calculated and plotted. For each solid, a few characteristic peaks related among others to the solid porous structure were obtained on the dependence curves (Fig. 13). As follows from the above presented investigations, the kinetics of liquid thermodesorption are influenced by the extent of interaction between a liquid molecule and the solid surface, the properties of the adsorbate molecule (e.g. its polarity), the character and type of surface, and the adsorption properties and porosity (type, size, specific surface area) [38]. In general, most solid surfaces are energetically, geometrically and structurally heterogeneous and porous. The above parameters dictate the properties of liquid films (mainly their thickness and structure), but the thermodesorption process under dynamic and quasi-isothermal conditions reflects the state of the films on the studied surface [75]. The dependences allow for determination of some interesting physicochemical parameters such as energy of adsorption and molecule bonding

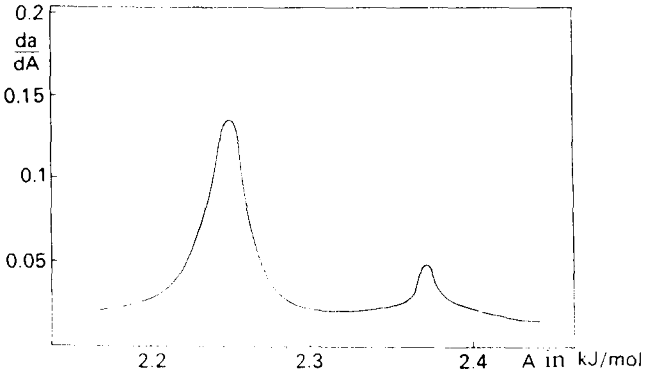


Fig. 13. Dependence of the adsorption potential distribution function $da/dA$ in relation to the amount of water adsorbed on a latex surface [74].

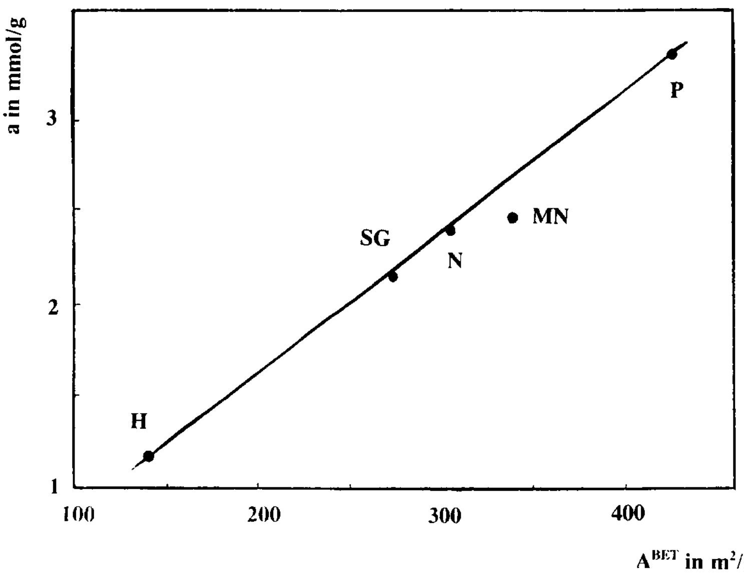


Fig. 14. Amount of water desorbed from silica gel surface as a function of specific surface area (samples: H, Hypersil; SG, Schuchardt SG; N, Nucleosil-100; MN, Kieselgel MN; P, Partisil) [79,80].

with the surface and distribution of adsorption energy and, on this basis, it is possible to determine the heterogeneous character of the studied surface by means of TA and computer techniques.

A high-resolution thermogravimetric analyzer (HR TGA), i.e., a TGA with automatically programmed temperature control, was used to study the thermodesorption of water, *n*-butanol, benzene and *n*-octane from aluminum oxides [76] and active carbons with different porosities and surface heterogeneities [77,78]. The measured weight-loss curves included steps which reflected the evaporation of the liquid from meso- and micropores and the thermodesorption of molecules from the carbon surface. The heights of these steps could be directly correlated to the adsorption and surface capacity, total porosity, microporosity and specific surface area of the samples [79,80] (Fig. 14), as well as giving information about the thermal stability of the liquid-solid system studied. In addition, the high-temperature steps of the HR TGA curves showed significant broadening arising from the microstructural and surface heterogeneities of the active carbons. The current studies of active carbons immersed in liquids have demonstrated the usefulness of the first derivative of the time-dependent weight-loss DTG curve for obtaining information about the total porosity of the solid surface (Fig. 15). In the case of benzene, the TGA and DTG curves are especially useful for characterizing the surface and structural heterogeneities, and for estimating the micropore volume of carbon samples because of the strong adsorption of benzene in the micropores. In addition, the DTG curves for the carbon samples exposed to water vapor provide information about the total number of active sites on the carbon [78] and also on silica gel [81] surfaces (Fig. 16).

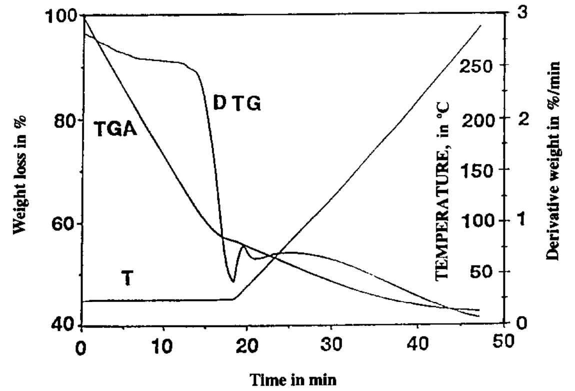


Fig. 15. TGA (thermogravimetric), DTG (first derivative of the time-dependent weight loss) and TA (temperature) curves for thermodesorption of benzene from active carbon [77].

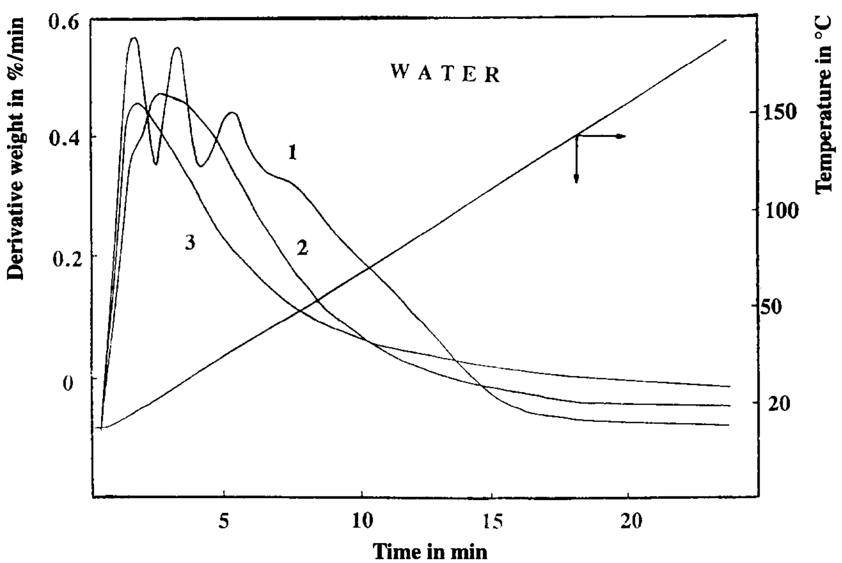


Fig. 16. Time-dependent weight-loss curves as a function of time for water thermodesorption from different active centers of silica gel surfaces (curve 1, LiChrosorb Si-60; curve 2, Nucleosil-100; curve 3, SG/7G) [81].

Recently [80], programmed thermodesorption studies of mixtures of two liquids (e.g. octane–benzene, propanol–benzene, propanol–decane, phenol–benzene) previously adsorbed on silica gel surface have been carried out. Inflection points (at least three on each curve) which correspond to desorption of the group of liquid molecules in an equal energetic state in the studied system are found on the Q-TG curves. Fig. 17 shows as an example the dependence of the amount of desorbed liquid on the composition of propanol–decane mixtures with which silica gel had

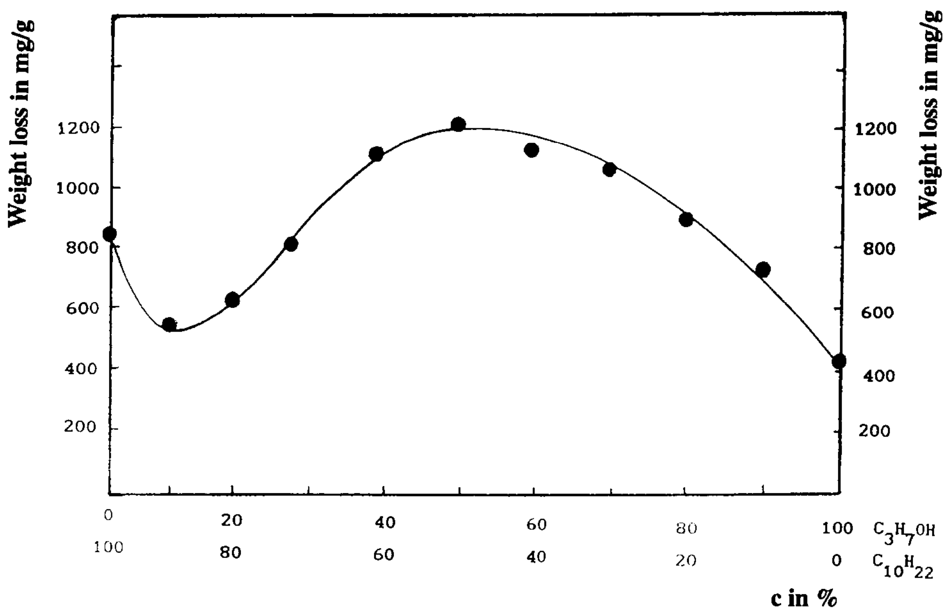


Fig. 17. Amount of liquid desorbed from silica gel surface as a function of solution concentration (from inflections related to "adsorption region" on Q-TG curves) [80].

earlier been in contact showing an inflection corresponding to the adsorption film being under the influence of surface forces. As follows from the figure, different amounts of liquid were desorbed from the sample depending on the percentage composition of the mixture. The amount depended on the type and extent of interaction between adsorbent and adsorbate and between the adsorbate molecules. It is worth noting that the presented dependence has a shape similar to that of isotherms of solutions obtained for similar systems. Studies of this type can contribute to the explanation of mechanisms and of the composition and structure of layers formed during the adsorption process of solutions.

## 5. DSC measurements

The heat effects corresponding to changes in water–solid sample systems with temperature can be studied by DSC, which is capable of monitoring phase [76,82] and structural [79,80] transitions of adsorbed films on microporous solids. Alumina samples exposed to saturated water vapor in a desiccator have been investigated by DSC over the range from −70°C to 650°C under controlled rate conditions. The resulting DSC curves (Fig. 18) have complex shapes with peaks related to the freezing (peak 1) and melting (peak 2) of different types of surface water at subambient temperatures, thermodesorption of physically adsorbed water molecules from the pores (peak 3) and the oxide surface (peak 4) and decomposition of

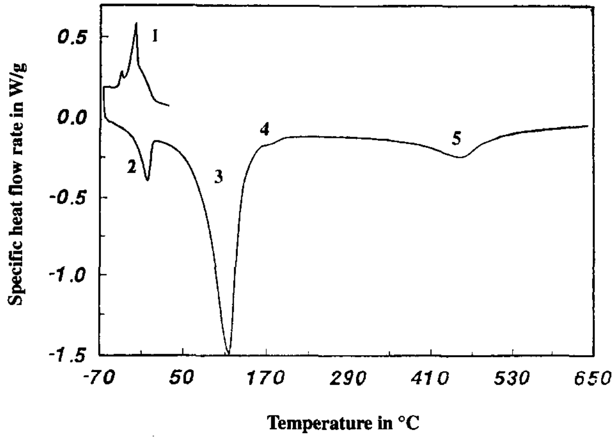


Fig. 18. DSC curve for the alumina sample Al-13 saturated with water vapor in a desiccator. The peaks 1–5 are described in the text [76].

hydroxyl groups (peak 5) at elevated temperatures. The shapes of the DSC peaks depend on the type of surface, and they can be used to obtain information about the surface and structural properties of the porous solids studied. For instance, the DSC peak 1 (Fig. 18) associated with freezing of the liquid adsorbate can be used to evaluate the pore size distribution by utilizing the relationship between the equilibrium temperature $T$ and the radius $r$ using the Gibbs–Duhem and Laplace equation [83]

$$T - T_0 = 2\gamma T_0/(\rho_w \chi r) \tag{4}$$

where $T_0$ is the normal melting temperature of ice, $\rho_w$ is the density of water at $T_0$, $\chi$ is the normal heat of fusion of ice per unit mass, and $\gamma$ is the interfacial tension.

The freezing temperature of adsorbed water is proportional to the pore radius [84]; the peaks at the lowest temperatures are associated with the freezing of water in fine pores [85], and their shapes reflect the structural heterogeneity of a given porous solid. For instance, alumina sample Al-9 (Fig. 19) has larger pores than sample Al-30 because its peaks appear at higher temperatures than for Al-30 (Fig. 20). Also, the more complex shape of the DSC curve for the Al-9 sample suggests that its structural heterogeneity is greater than that of Al-30 [76].

## 6. Summary

Based on the studies using controlled rate TA, it can be stated that this method is simple, useful and effective in evaluation of the interactions of adsorbent and adsorbate and in characterizing the physicochemical properties of both a surface (particularly its energetic state and porosity) and liquid films. The adsorption and desorption processes depend on the surface physicochemical properties of the solid

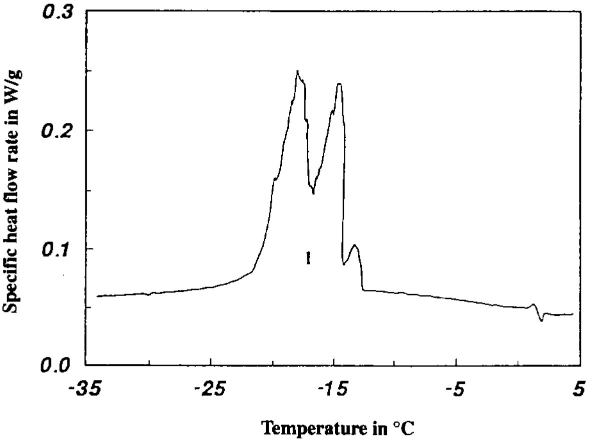


Fig. 19. The part of the DSC curve related to the freezing of water in the mesopores of alumina Al-9 sample [76].

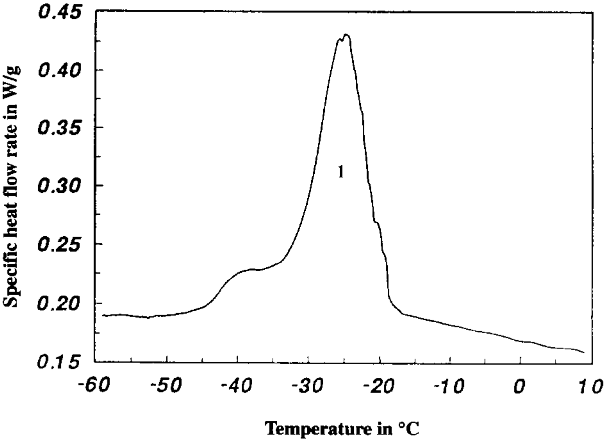


Fig. 20. The part of the DSC curve related to the freezing of water in the mesopores of alumina Al-30 sample [76].

studied and the wetting liquid surfaces, and different series of TGA, DTA, DTG, Q-TG and DSC curves which reflect the state of molecular interactions and the particular liquid–solid system have been obtained. The results of investigations have shown that the solid surface causes significant changes of properties, particularly in the structure and thickness of the layers under the liquid surface. It is reflected by the recently reported studies that the thermodesorption process proceeds in a "stepwise" but not in an exponential way, which reflects a discontinuous change of adsorption properties close to the surface layers depending on the distance and results from the difference in the liquid–liquid and liquid–solid interactions. The process becomes more pronounced with increased polarity of the molecules of the wetting liquid as well as the heterogeneous properties and developed specific surface area of the solid. This phenomenon becomes more intense with decreases in the polarity of the wetting liquid molecules and the heterogeneous character of the solid surface.

From the analysis of the TGA, DTA, DTG, Q-TG and DSC curves, the properties of liquids present on the porous surfaces (e.g. in macro-, meso-, micro- and submicropores) are determined. The derivative time-dependent weight-loss DTG curves are very important because they contain information about the surface capacity, the nature of active centers, specific surface area, discontinuous change of adsorption layer properties, and changes in the mechansim of the wetting process due to interactions between surfaces and the heterogeneity of solid surfaces. However, the derivative of mass loss in relation to temperature is connected with the distribution function of the activation energy of desorption. The function characterizes the heterogeneity of adsorbents due to micropores (structural heterogeneity) and that due to the existence of various adsorption centers (surface heterogeneity). The DSC curves obtained during controlled sample cooling and heating are associated with the water freezing process in pores, and their shapes at subambient temperatures reflect the structural heterogeneity of the sample, whereas the curves obtained at elevated temperatures provide information about surface heterogeneity and supplement the results obtained from TGA measurements. Moreover, the DSC peaks are related to heat effects associated with the phase and structural transitions in the surface water layers.

The methods presented are very quick and convenient in studies of heterogeneity with respect to different adsorbates. It is possible to use any liquids and their mixtures having different properties (polar and nonpolar) and to study surface heterogeneity in relation to these liquids and the mechanism of adsorption from solutions. It is also possible to study the effect of surface heterogeneity (by chemical and physical modification of sorbents) on the wettability of solids, formation of liquid films, and their structure and thermal stability. These problems are very important in many fields. The method enables studies on how, e.g. the presence of water on a surface changes its surface properties in relation to other liquids and how it affects their interactions. It is possible to determine the properties of films and of phase and structure transitions at different humidities and the degree of hydrophobic and hydrophilic character of the surface. The method allows a study of the effect of small quantities of substance (modifiers) on the stability of a film on a surface. The method of controlled TA is convenient for evaluation of changes in the properties of a thermally treated adsorbent (change of structure and heterogeneity). For instance, it is possible first to heat the sorbent and then, after cooling, to apply liquids to it and to observe changes in its properties. It should be noted that measurements can be made in atmospheres of different gases.

The results obtained so far show the extensive applicability of these methods in determination of the physicochemical properties of solid surfaces and adsorbed liquid films, particularly in calculations of surface free energy, adsorption potential distribution, activation energy of adsorbed molecules on a surface and determination of surface and structural heterogeneity using a computer technique. The above examples show the wide applicability of the method in studying liquid films and surface properties of solids, their heretogeneity and their effect on the thermal stability of adsorbed liquid films. After appropriate modification, a derivatograph can be used in adsorption and calorimetric studies of liquid–solid systems in addition to its conventional application. The outlined methods of study can be competitive with the traditional methods because of the speed and accuracy of obtaining data and the simplicity of experimental operation.

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