Journal of Thermal Analysis, Vol. 31 (1986) 1055–1061

DETERMINATION OF LIQUID ADSORPTION AND DESORPTION ON AND FROM SOLIDS BY MEANS OF THE DERIVATOGRAPH

Part III. Determination of water adsorption and desorption heats on silica gel by derivatographic measurements

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(Received May 25, 1985)

This paper presents a method for calculation of the adsorption and immersion heats of water on a silica gel surface from the DTA curve obtained with a modified derivatograph. The adsorption and desorption heats have also been determined. The relationship between the adsorption heat and the amount of water adsorbed is presented.

The immersion of an outgassed solid in a liquid is accompanied by the liberation of heat called the immersion heat. Thus, the wetting process is an exothermic one and during this process a change, ΔH_i; takes place in the system enthalpy [1, 2]. Hence, the immersion heat is directly dependent upon the total adsorption heat, ΔH_a, liberated during the saturation of the solid by vapour [3]. The ΔH_a value refers to the process in which 1 g of the outgassed solid is stored until equilibrium with the saturated vapour has been obtained. The relationship between ΔH_i; and ΔH_a can be found via the Hess law. Let us consider the wetting process as a two-step process [3].

First step: The condensation of n moles of vapour into liquid during the wetting of 1 g of solid. The change in enthalpy is:

$$\Delta H = -n\Delta H_0 - \Delta H_i; \tag{1}$$

where ΔH_0 is the latent heat of liquid evaporation.

Second step: The adsorption of n_1 moles of vapour on the solid surface until the equilibrium state has been attained. The change in enthalpy, ΔH_1, is:

$$\Delta H_1 = -\Delta H_a \tag{2}$$

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After the adsorption process, condensation of the residual $(n-n_1)$ moles of vapour occurs. The enthalpy change corresponding to this phenomenon is:

$$\Delta H_2 = -(n-n_1)\Delta H_0 \tag{3}$$

Wetting of the solid covered with the liquid film then takes place. The amount of heat liberated during this step, q_1, is relatively small. Hence, the change in enthalpy of the system, ΔH_3, is:

$$\Delta H_3 = -q_1 \tag{4}$$

According to the Hess law, the total heat change remains the same in each step. Thus:

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{5}$$

or

$$-n\Delta H_0 - \Delta H_i = -\Delta H_a - (n-n_1)\Delta H_0 - q_1 \tag{6}$$

and thus:

$$\Delta H_i = (\Delta H_a - n_1\Delta H_0) + q_1 \tag{7}$$

$(\Delta H_a - n_1\Delta H_0)$ is the net integral heat of adsorption. The value of q_1 is relatively small and can be compared to ΔH_1 or ΔH_2. If the adsorption isotherm tends asymptotically to $p/p_0 = 1$, then the value of q_1 must equal zero (by thermodynamic arguments). When the isotherm intersects the ordinate under a particular angle, then q_1, though small, will still be well defined. From these facts it appears that the immersion heat is equal to or approximates to the net integral heat of adsorption.

The integral adsorption heat is conditioned by the differential adsorption heat q according to the following relation:

$$\Delta H_a = \int_0^{n_1} q \cdot \mathrm{d}n_1 \tag{8}$$

The immersion heat depends on many factors, such as the nature of the surface, its structure, and the method of preparation of the solid sample. It has been concluded that the immersion heat is directly proportional to the solid specific surface area [2, 3].

A calorimeter is usually used for measurement of the adsorption heat [4–7]. A thin-wall glass ampoule with a strictly-defined amount of solid is immersed in the liquid contained in the calorimeter. After the temperature has been established, the ampoule is broken. In the knowledge of the calorimeter heat capacity, the amount of heat liberated during the wetting process can be calculated from the temperature change caused by the adsorption.

This part of the paper describes a method of calculation of the adsorption heat and the immersion heat from the DTA data measured with a derivatograph [8, 9].

Experimental

The measurements of water adsorption and desorption on the silica gel surface were carried out with a Q–1500 D derivatograph (MOM, Hungary). The experimental methods and silica gel parameters were reported in previous papers (8, 9].

Results and discussion

The water adsorption heats on the silica gel surface were calculated from the DTA peaks presented in Fig. 1, and Fig. 2 in an earlier paper [8]. Curve BC, obtained during the adsorption heat measurements by means of the calorimetric method, has a typical shape.

The adsorption and desorption heats of water on the silica gel surface were calculated by a comparative method. First the apparatus had to be calibrated. In order to do this, a strictly defined amount of distilled water was deposited from a microsyringe onto a suitable balance pan of the modified derivatograph [8]. Water was then desorbed from the balance pan by means of a stream of dry nitrogen at 20°.

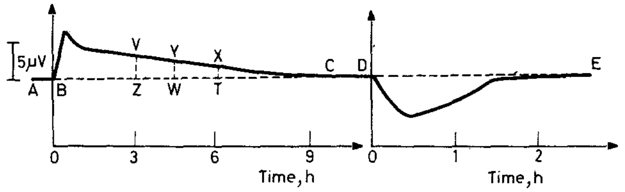

Fig. 1 DTA curve corresponding to the heats of adsorption (sector BC) and desorption (sector DE) of water vapour on silica gel at 20°

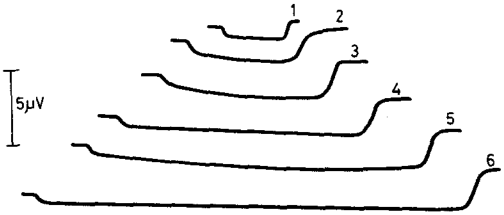

Fig. 2 DTA curves of water evaporation from the balance pan for different sample weights: 1 – 5 mg, 2 – 10 mg, 3 – 20 mg, 4 – 30 mg, 5 – 40 mg and 6 – 50 mg

Some DTA curves are presented in Fig. 2. From the peak surface area S (mm^2) and the amount of desorbed water m (mg), the relationship between S and m was established and plotted in Fig. 3. ΔH_0 = 43.89 kJ is needed to evaporate 1 mole of water at 20°. Figure 4 presents $\Delta H = f(S)$, the dependence which related the DTA

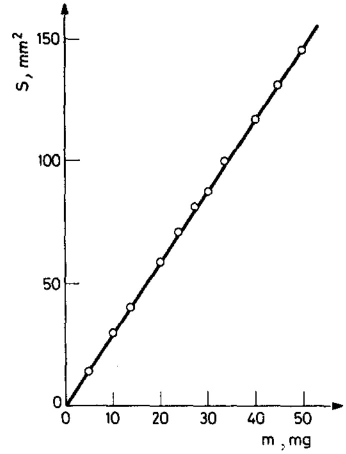

Fig. 3 Dependence of peak surface area on the amount of desorbed water

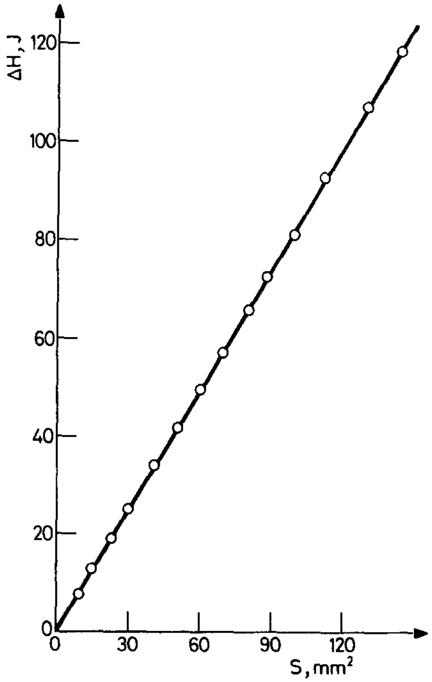

Fig. 4 Relationship between the heat values and area of DTA peaks

peak surface area to the heat needed for evaporation of a given amount of water. The dependences shown in Figs 3 and 4 may be presented analytically in the form of the following equations:

$$S = 2.941\ m \tag{9}$$

and

$$\Delta H = 0.82783\ S \tag{10}$$

From Eqs (7) and (10) and the peak surface areas (Fig. 2), we were able to calculate the heat values ΔH_a and ΔH_i accompanying the adsorption and desorption of water on the silical gel surface. Since the adsorption isotherm of water on silica gel (Fig. 2 in [9]) approaches asymptotically to $p/p_0 = 1$, the value of q_1 in Eq. (7) must equal zero. The results of the calculations are presented in Table 1.

Table 1 The reproducibility of the data

	Amount of the water		The peaks surface area, mm^2	Heat of adsorption, kJ/mol	Heat of immersion kJ/mol
	mg	mmol/g			
Adsorption	38.8	61.6	327.0	105.95	103.25
Desorption	37.4	59.4	217.1	86.45	83.84

From the data in Table 1 it appears that the adsorption heats are greater than the desorption heats. This is due to the irreversibility of the adsorption process under the given measuring conditions. On the silica gel sample, which was previously dried at 300°, some water about 2.2 mmol/g is adsorbed irreversibly. This is the bonded water, which cannot be desorbed at 20° by a dry nitrogen stream. Desorption occurs only when the sample is heated up to 300° (see [8, 9]). Some of the water can be utilized for reconstruction of the surface hydroxyl groups removed from the surface when the sample was heated before adsorption. This is why the surface area of the adsorption peak and therefore the adsorption heat too is greater than that for desorption.

The relationship between the adsorption heat and the amount of water adsorbed on the silica gel is presented in Fig. 5. In order to obtain this relationship, curve BCB (Fig. 1) was integrated graphically in the following way. The area BCB corresponds to the integral adsorption heat $\Delta H_a = 105.95$ kJ/mol, or in terms of the sample weight $\Delta H_a = 7.73$ kJ/g. The individual areas, e.g. XTC, YWC, VZC, ..., correspond to the heat values ΔH_{a1}, ΔH_{a2}, ΔH_{a3}, ... liberated during the adsorption of a_1, a_2, a_3, ... mmoles of water on 1 g silica gel sample. The relationship presented in Fig. 5 is similar to that obtained by Ovtshcharenko [10] illustrating the dependence of the wetting heat of bentonite on the water vapour

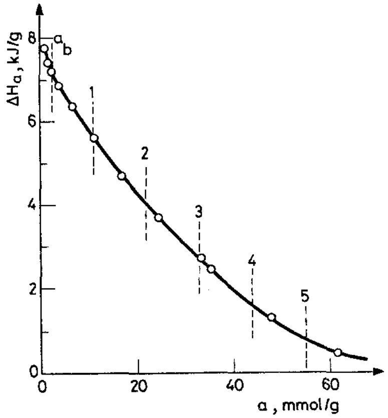

Fig. 5 Change of the adsorption heat in relation to the amount of water adsorbed on silica gel. Statistical monolayers of adsorbed water are denoted on the curve.

pressure p/p_0. It appears from this Figure that the adsorption heat is greatest when the first adsorption layers are being formed. The curve presented in Fig. 5 has a distinct inflection, corresponding to the adsorption of bonded water with a_b = 2.2 mmol/g. The curve then approaches the abscissa asymptotically.

Conclusion

The above-mentioned measurements and calculations indicate that the modified derivatograph can be used for the simultaneous determination of the adsorption and immersion heats. An important advantage of this method is that the adsorption and desorption heats can both be measured in one experimental run. These measurements cannot be performed in the conventional calorimetric method.

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Zusammenfassung — Eine Methode zur Berechnung der Adsorptions- und Immersionswärmen von Wasser an Silikagel aus den mit einem modifizierten Derivatographen gemessenen DTA-Kurven wird beschrieben. Adsorptions- und Desorptionswärmen wurden bestimmt. Die Beziehung zwischen der Adsorptionswärme und der Menge des adsorbierten Wassers wird angegeben.

Резюме — Исходя из кривых ДТА, полученных с помощью модифицированного дериватографа, представлен метод вычисления теплот адсорбции и погружения воды на поверхности силикагеля. Определены также теплоты адсорбции и десорбции. Показана взаимосвязь между теплотой адсорбции и количеством адсорбированной воды.