Journal of Thermal Analysis, Vol. 30 (1985) 1115–1119

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

Part I. Derivatograph for measurements of adsorption and desorption at a constant temperature

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(Received February 22, 1985)

A modofied Q–1500 D derivatograph (MOM, Hungary) allowing measurements of sample weight changes at constant temperature is described. The sample weight changes measured were due to the adsorption and desorption of liquid vapour flowing in an inert gas stream through the measuring cell at constant temperature. This apparatus permits the utilization of thermal analysis for adsorption investigations.

Sample weight changes may be measured with a derivatograph by either nonisothermal or isothermal methods. In the nonisothermal method [1–4], the sample and the reference substance are simultaneously heated under the same conditions. The temperature increase gives rise to physical and chemical transitions, such as evaporation [5], melting, structural changes, decomposition, oxidation, etc., and consequently the sample weight changes.

In the isothermal method [6–8], the sample weight changes caused by its heating at constant temperature are recorded until constant weight is obtained. The sample weight change curves are determined for chosen temperature ranges, e.g. 350–450° [7] or 110–265 [8]. Before measurements, the samples e.g. zeolites, are wetter with water, placed in a crucible and heated at a constant temperature. Under isothermal conditions, the measurements are usually carried out at temperatures higher than the boiling point of the liquid in the sample investigated.

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The object of this paper is the application of a derivatograph to investigate liquid vapour adsorption and desorption on and from solid surfaces at constant temperature. The derivatograph was fitted with appliances necessary for these investigations.

Experimental

Apparatus

A Q–1500 D derivatograph (MOM, Hungary) was fitted with appliances permitting the saturation of an inert gas with the vapour of the liquid investigated, the introduction of gases into the measuring cell, and the attainment of a constant temperature in the measuring cell [9]. Before measurements, the reference holder was removed from the measuring cell in order to prevent the adsorption and desorption of liquid vapour on and from it. A special sample holder was placed in the measuring cell.

Figure 1 A presents a block diagram of the apparatus. The unit permitting saturation of an inert gas with the liquid vapour consists of an inert gas (nitrogen) bottle (1) connected to a flowmeter (2), a multi-way valve (3), a saturator filled with the liquid investigated (4), a cooler (5) and the measuring cell (11) of the thermobalance (8). Saturator (4) is heated by a sand bath (6). Cooler (5) is connected to an ultrathermostat (7) producing vapour at the measuring

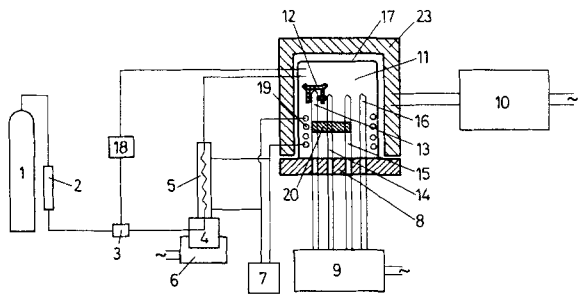

Fig. 1 A Experimental set-up of the derivatograph for the determination of liquid vapour adsorption and desorption on and from solids. 1 – nitrogen source, 2 – gas flow meter, 3 – multi-way valve, 4 – saturator, 5 – excess vapour rectifier, 6 – sand bath, 7 – ultrathermostat, 8 – thermobalance, 9 – recorder, 10 – power supply, 11 – measuring cell, 12 – sample holder, 13, 15 – ΔT thermocouple, 14 – thermocouple of program Q, 16 – temperature thermocouple, 17 – quartz jacket, 18 – nitrogen drying washers, 19 – metal coil, 20 – weight, 21 – screw, 22 – tube, 23 – furnace

temperature. The constant temperature in the measuring cell is obtained by circulating water from the ultrathermostat through a metal coil (19).

Figure 1 B presents an oblong section and Fig. 1 C presents a cross-section of the sample holder (12), a rectangular silver pan (2.5 × 3 cm), the edges of which are curved in order to retain the sample. The pan is equipped with a 5 mm long tube (22) and a screw (21) allowing its fixation to the measuring thermocouple (13) (Fig. 1 A).

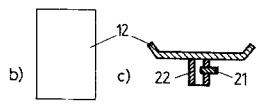

Fig. 1 B Oblong section of sample holder

Fig. 1 C Cross-section of sample holder

Materials

Silica gel (Machery Nagel, Germany) for chromatographic columns, with a particle size of 0.15–0.3 mm and a surface area of 467 m^2/g, was used. The surface area was determined with a Sorptomatic 1800 apparatus (Carlo, Erba, Milan, Italy).

Procedure

Before the measurements, a silica gel sample (35 mg) was placed on the derivatograph sample pan and was heated up to 300° in order to remove volatile substances (especially hygroscopic water) from its surface (Fig. 2, T and TG curves, sectors AB). The furnace was then elevated and the measuring cell was cooled to 20° without removal of the quartz jacket (17). During the heating and cooling process, dry inert gas (nitrogen) was passed through the measuring cell. The quartz jacket and the continuously flowing dry nitrogen protected the sample against the influence of the atmosphere. The position of the multi-way valve was then changed and nitrogen saturated with water vapour was passed through the measuring cell. The nitrogen was saturated with water vapour in the following way. Nitrogen from bottle (1) was passed through saturator (4), containing water preheated to about 60°. The preheated mixture of nitrogen and water vapour was cooled in cooler (5) until the measurement temperature (20°) was reached. The temperature was regulated by thermostat (7). The water vapour excess was condensed in cooler (5) and collected in saturator (4).

As a result of the flow of nitrogen saturated with water vapour through the measuring cell, water was adsorbed on the silica gel sample. The derivatograph

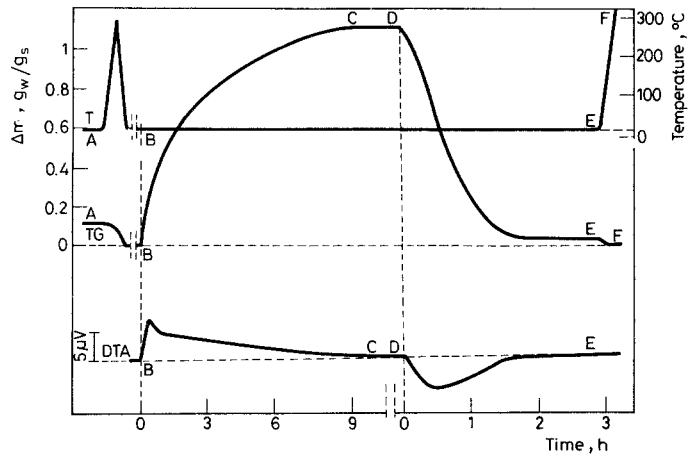

Fig. 2 T, TG and DTA curves corresponding to adsorption and desorption of water vapour on and from silica gel at 20°.
T curve: peak AB – sample heating to 300° and cooling to 20°; sector BE – constant temperature (20°) during measurement; sector EF – sample heating to 300° after the desorption process.
TG curve: sector AB – evaporation of hygroscopic and bound water; BC – adsorption of water; CD – plateau; DE – desorption of water; EF – thermal desorption of bound water.
DTA curves: sector BC – corresponds to the heat of adsorption of water on the silica gel; CD – plateau; sector DE – the heat of desorption of water from the silica gel surface

recorder plotted the TG curve of sample weight increase vs. time (Fig. 2, sector BC). As a result of the adsorption on the sample, a small amount of adsorption heat was liberated and hence the temperature of the sample was somewhat higher than ambient temperature. The recorder simultaneously plotted the DTA curve (Fig. 2, sector BC). After complete sample saturation (adsorption equilibrium, plateau in Fig. 2, sector CD), the gas + water vapour mixture inlet was stopped and pure dried nitrogen was introduced again into the measuring cell. Water desorption from the sample then occurred. The recorder plotted the weight in the form of a TG curve (Fig. 2, sector DE). Water desorption was accompanied by the absorption of a small amount of heat and yielded an endothermic peak in the DTA curve (Fig. 2, sector DE). The derivatograph furnace was then lowered and the sample was heated up to 300°, when the water bound by the silica gel underwent thermal desorption (Fig. 2, T and TG curves, sectors EF).

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Zusammenfassung — Es wird ein modifizierter Derivatograph vom Typ Q-1500 D (MOM, Ungarn) beschrieben, der die Messung von Veränderungen des Probengewichtes bei konstanter Temperatur ermöglicht. Die adsorption und Desorption einer bei konstanter Temperatur in einem inerten Gasstrom durch die Meßzelle strömenden gasförmigen Substanz wird durch Messung des Probengewichtes verfolgt. Eine Apparatur für thermische Analyse wird damit zu Adsorptionsuntersuchungen verwendet.

Резюме — Описан модифицированный дериватограф типа Q-1500 Д (МОМ, Венгрия), позволяющий проводить измерения изменений веса образца при постоянной температуре. За весовыми изменениями следует адсорбция и десорбция паров, находящихся в потоке инертного газа и пропускаемых через измерительную ячейку при постоянной температуре. Аппаратура дает возможность использовать метод термического анализа для исследования адсорбции.