

AUTOMATIC GRAVIMETRIC APPARATUS FOR RECORDING THE ADSORPTION ISOTHERMS OF GASES OR VAPOURS ONTO SOLIDS*

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ABSTRACT

The assembly described was built with the aim of obtaining high resolution and precision, together with automaticity. It was designed around a symmetrical commercial vacuum microbalance (Setaram), its main features being the following:

(1) Controlled "residual" vacuum during outgassing of the sample.

(2) Two possible procedures for the introduction of the adsorbate: either a conventional — but automated — point by point procedure (with discontinuous introduction of gas or vapour) or a continuous procedure, specially suited for high resolution work.

(3) Measurement of pressure (0–1 atm) by a silica Bourdon gauge (Texas Instruments) of 10^{-5} accuracy.

(4) Direct recording of the isotherms on a XY recorder.

(5) Constant level (± 0.5 mm) cryogenic bath (liquid nitrogen or argon) of low consumption (4 liters per 15 hours).

(6) Liquid thermostat for adsorption temperatures between -30 and $+100^\circ\text{C}$.

(7) Temperature control (up to 50°C) of the whole assembly (manifolds, balance, gauges) allowing to handle condensable vapours.

Several examples are given, illustrating the versatility and resolution of the system. For instance, it allowed to detect, for the first time, a distinct substep at the top of the nitrogen/graphite and argon/graphite isotherms at 77 K. This is now explained by a sudden localization or "freezing" of the monolayer near its completion.

INTRODUCTION

Our starting point was a number of calorimetric recordings concerning adsorption of nitrogen or argon onto graphite at 77 K and which could not be interpreted even with the help of the numerous isotherms already published for these systems. On

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our calorimetric recordings indeed we detected a well-defined exothermal peak close to the completion of the monolayer, whereas no anomaly appeared, on the isotherms, at the corresponding place (i.e., at the top of the first step). All these isotherms had been plotted by a volumetric technique and with a point by point procedure. We therefore decided to build an adsorption equipment able to lead, if possible, to a higher resolution. We also wanted a good accuracy in order to perform the often difficult comparison between the calorimetric and the isosteric procedures for determining the derived enthalpy of adsorption (or "isosteric heat"). For these reasons, the assembly finally built includes the following features:

- outgassing system under constant "vacuum",
- device for automatic use of the conventional procedure of discontinuous introduction or extraction of gas,
- device for use of a high-resolution procedure (as will be seen) of continuous introduction or extraction of gas,
- direct recording of the isotherm.

DESCRIPTION

Figure 1 shows the general arrangement of the system. The symmetrical balance (Setaram MTB 10-8) is connected:

- to the vacuum pumps (oil diffusion pump and two-stage rotary pump) and liquid nitrogen trap,
- to a gas manifold described below,
- to three pressure gauges (a Penning gauge for the 10^{-6} to 10^{-3} torr range, a thermocouple gauge for the 10^{-3} to 1 torr range and a Texas fused silica Bourdon tube automatic gauge for the 10^{-2} to 1000 torr range) working independently from one another.

The sample is placed in a deep blackened cylinder (height: 60 mm, external diameter: 14 mm; material: anodized aluminum; weight: 3.9 g) which is never completely filled (the thickness of the sample layer is usually only a few millimeters) but which acts as a "radiator". This solution was possible because of the 14 g maximum load of the balance, which leaves nearly 10 g for the sample. The cylinder is itself surrounded with a blackened aluminum sheet lining a stainless-steel tubing (height: 245 mm; internal diameter: 19 mm) itself attached (by Leybold vacuum fittings) to the balance. With this arrangement, when the liquid nitrogen bath is used, the temperature difference between the sample and the bath is about 0.2 K provided the pressure of the gas around the sample is higher than $5 \cdot 10^{-2}$ torr¹.

During the outgassing, the heating of the symmetrical furnace (one side of which is represented on Fig. 1) is controlled by the low pressure gauges (Penning gauge or thermocouple gauge) in order to keep constant both the residual pressure during outgassing (usually in the $5 \cdot 10^{-5}$ to 10^{-3} torr range) and the rate of outgassing, following the lines of a method described elsewhere². One definite advantage of controlling the rate of outgassing is that any "spurting" of the sample out of the

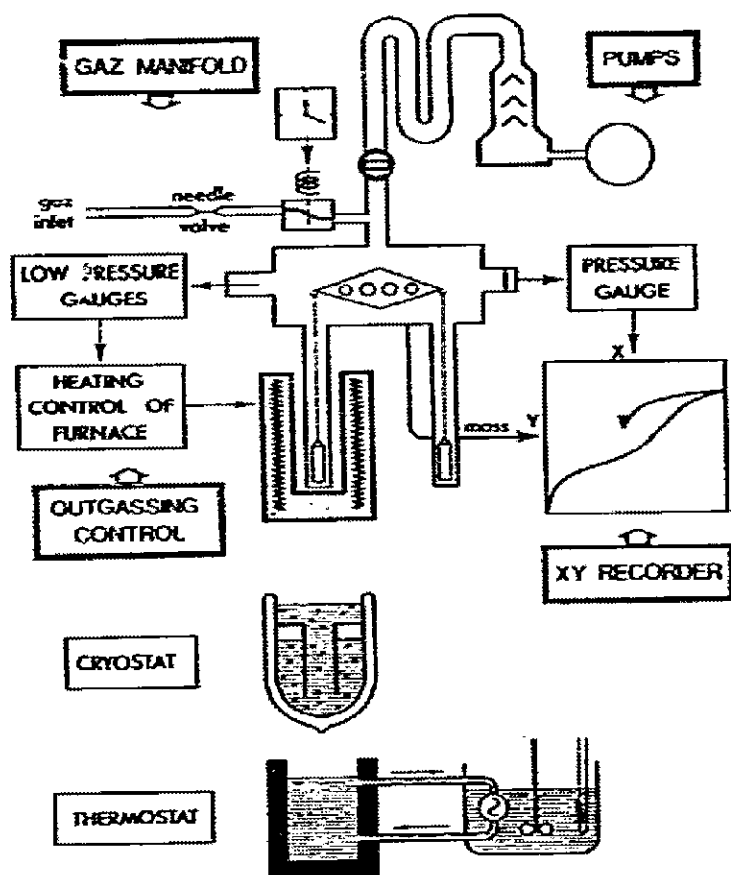


Fig 1

Fig. 1. General arrangement of the system.

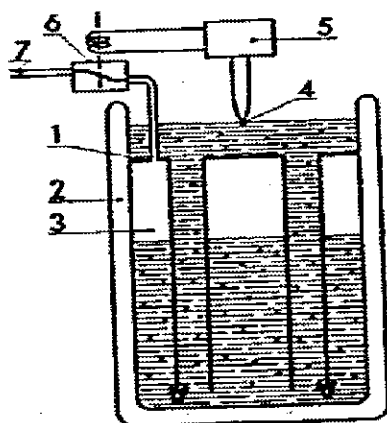


Fig 2

Fig. 2. Cryostat with level control.

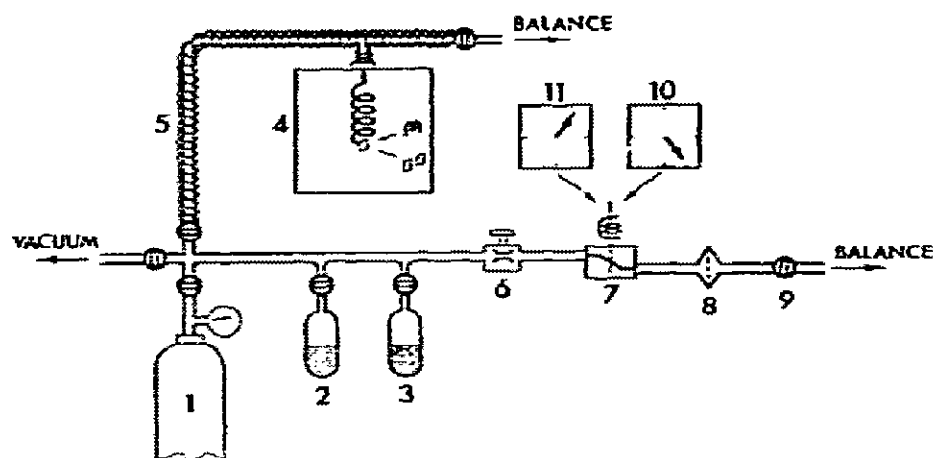


Fig 3

Fig. 3. Gas manifold.

cylinder may be avoided. The furnace is designed for a maximum temperature of 500°C.

After outgassing, the symmetrical furnace may be replaced by a symmetrical liquid thermostat (for temperatures ranging between -30 and $+100^{\circ}\text{C}$) or by a symmetrical liquid nitrogen (or argon) bath. A constant level device was designed in order to keep the cryogenic liquid at its higher level³. Its principle is given on Fig. 2: a double bottom 1 is tightly inserted within a 5-l stainless-steel Dewar vessel 2; the natural losses of the Dewar are usually sufficient to produce, under the double bottom, a vapour phase 3 which exerts a pressure on the cryogenic liquid, making it going up (following the arrows) through the two tubes (or wells) welded to the double-bottom. As soon as the upper level of the cryogenic liquid reaches the sensor 4 (a diode), the electric bridge and amplifier 5 open the valve 6, allowing the vapour phase to escape slowly through a diaphragm 7, and therefore lowering the upper liquid level. The great difference with the usual constant level devices (using an external supply of cryogenic liquid) is that the control loop may operate as often as necessary (i.e., 1 cycle per minute for instance) without increasing the cryogenic liquid consumption and without disturbing the temperature of the bath. The level is controlled within ± 0.5 mm and the liquid nitrogen consumption is 4 l per 15 h. After this time the Dewar must be refilled (a 24-h autonomy system of identical design but of higher capacity was also built for another purpose). The two wells allow of course to deeply immerse the two tubes of the adsorption balance.

The gas manifold is represented on Fig. 3. It may be connected:

- to the gas supply 1 or to the vapour supplies 2 and 3; the latter are immersed either in the air thermostat in which the gas manifold and the balance are encased (the temperature may be set between 30 and 50°C) or in the liquid thermostat (-30 to 100°C);
- to the Texas gauge 4, through the temperature-controlled tube 5;

– to the balance, through the leak valve 6 (Granville-Phillips variable leak), the electromagnetic valve 7, the sintered metal filter 8 and finally through the manually operated valve 9.

The use of the discontinuous adsorption (or desorption) procedure only needs to set the opening time (timer 10) and the closure time (timer 11) of the electromagnetic valve 7; the cycle is then repeated indefinitely. The use of the continuous procedure needs to keep the electromagnetic valve open and to set the Granville-Phillips valve in such a way as to complete the adsorption experiment within the desired time. We may notice that the internal volume of the balance (about 2 l) is large enough to lead to a continuous increase of pressure, independent from the amount of gas adsorbed by the sample, which is comparatively small. The rate of increase of the pressure may be set as low as 2 torr per hour.



Fig. 4. General view of the apparatus. Left cabinet, from top to bottom: gas manifold, liquid thermostat surrounding the vertical tubes of the balance (behind the transparent door closing the air bath), balance electronics, temperature controllers, timers, vacuum gauges, Texas gauge. Right cabinet: inside, rotating pump and thermostat-cryostat; on the top, X-Y recorder.

The XY recorder (Sefram TRP) is usually connected to the mass signal (Y-axis) and to the pressure signal from the Texas gauge (X-axis). The mass changes may be recorded between 1 and 40 mg full scale and the pressure changes may be recorded between 10 and 1000 torr full scale. From 25 torr onwards, the pressure signal is delivered through a retransmitting potentiometer. For the lower pressures, the output signal of the unbalanced bridge may be used and avoids the recording of small steps corresponding to the loops of the resistor. The pressure calibration of the recording is performed by reading the pressure on the meter with a resolution of ± 5 mtorr. During the outgassing, the X-axis of the recorder is fed with the thermocouple signal from the furnace, allowing to record a conventional TG trace (mass vs. temperature). A general view of the apparatus is given in Fig. 4.

EXAMPLES

Several typical isotherms recorded with the continuous procedure are reported on Fig. 5. Recording 5a is relevant to the problem mentioned in the Introduction and concerns the nitrogen/graphite system at 77 K. The specific surface area of the sample was $7.8 \text{ m}^2\text{g}^{-1}$ and 0.7 g of sample was used. The complete adsorption isotherm may here be recorded in less than 5 h (same situation as for Ar/graphite system (I)). The sensitivity of the system allowed to expand the part of the isotherm

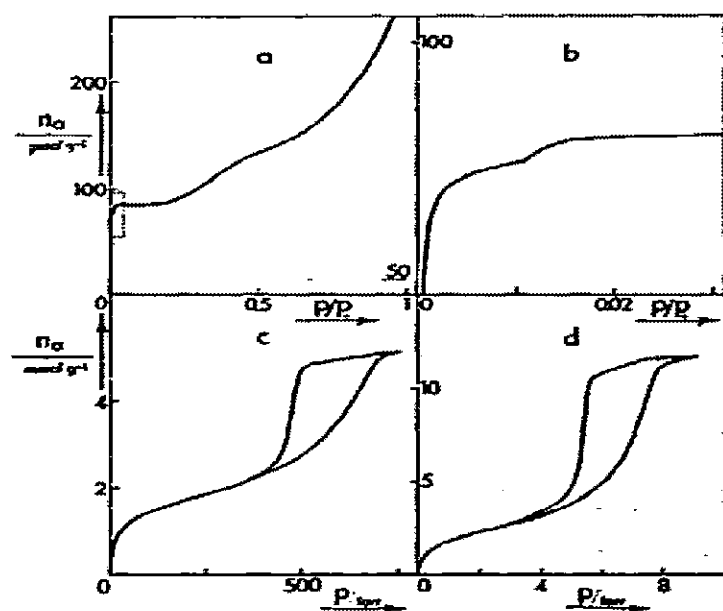


Fig 5

Fig. 5. Isotherms recorded with the "continuous" procedure. a = nitrogen/graphite, 77 K; b = same conditions but higher recording sensitivity; c = nitrogen/Vycor glass, 77 K; d = water/Vycor glass, 9.5°C.

enclosed in the rectangle in order to get the recording shown in Fig. 5b: a sub-step very clearly appears at the top of the main step of the isotherm. This sub-step was interpreted by a sudden modification of the adsorbed monolayer, changing from a bidimensional hypercritical fluid state to a localized bidimensional state⁴.

Figure 5c concerns adsorption of nitrogen, at 77 K, on a 42-mg sample of mesoporous Vycor glass. In such a case, the experimenter first has to set the conditions for recording the adsorption branch and, later, to cut off the gas supply and to begin pumping — always through the Granville-Phillips valve — in order to record the desorption branch of the isotherm. The latter smoothly reaches the adsorption branch, indicating a good general working of the system.

Figure 5d concerns adsorption of water, at 9.5°C, on the same adsorbent as formerly. The pressure range falls from 760 torr (Fig. 5c) to 10 torr (Fig. 5d) with no detectable loss of resolution. This isotherm was recorded in 5 h.

Nevertheless, we must point out one limitation of the method in the case of low-temperature adsorption: because the temperature of the sample is slightly higher than that of the cryostat (we know, from preliminary measurements that, in our assembly, the difference is 0.2 K¹), then the normal three-dimensional condensation never takes place on the sample itself, but on the inner walls of the surrounding tube which is itself directly immersed in the cryostat. It follows that the upper part of the hysteresis loop, such as recorded with a "free" gravimetric system (where the sample is not brought in mechanical contact with the cryostat) must be contemplated with caution. On the other hand, the same "free" gravimetric system has a very high versatility (pressure range and temperature range) and resolution (specially with the "continuous" procedure) and also has a satisfactorily high accuracy ($\pm 1\%$ of the amount adsorbed) in so far as the adsorption of the first layers is concerned.

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