

## TECHNIQUES FOR STUDYING ADSORPTION OF VAPOURS ON LOW SURFACE AREA SOLIDS

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**Abstract.** Some specialized volumetric and gravimetric techniques successfully used for studying adsorption of vapours on low-surface area solids, have been reviewed along with the necessary precautions to be taken during the experimental work. The piezogravimetric method has been evaluated in particular stating its merits, demerits and limitations.

Adsorption phenomena occupies a very special place in surface science and it has long been under intensive and comprehensive study. It is widespread and plays an extremely important role in catalysis, and in many theoretical and practical problems. Even so, the progress in this field, in general, has been quite limited—the experimental side being a little brighter.

It must be mentioned here that the present review by no means is an exhaustive one, but rather it is intended to serve as a guide in the choice of a method suitable for a given type of problem. Thus, it does not specifically touch any special cases of physical and chemical adsorptions, but includes some methods which have been used to investigate the adsorption in general, on low area solids.

There are a large number of methods available for studying adsorption, but a few specialized techniques used are reviewed here emphasizing various precautions that must be taken when adsorption data on low-specific surface adsorbents are required.

Techniques of measuring adsorption can conveniently be classified as (a) volumetric methods, in which the extent of adsorption at a fixed temperature, is assessed by means of simultaneous determinations of the pressure and volume of the fluid adsorbate, and, (b) gravimetric methods, in which the mass adsorbed is measured, directly or indirectly, at different pressures. The means whereby the mass adsorbed is determined varies from technique to technique.

*Outgassing.* Any procedure designed to study adsorption, whether this be physical adsorption or chemisorption, must be based upon sound vacuum techniques. This is necessary for two reasons: first, there is the need to remove extraneous species from the gas-phase, second, so far as possible, one wishes to remove previously adsorbed species from the adsorbent surface. For this reason the process of outgassing should be accompanied by pressure measurements. Complete outgassing could require days of pumping and heating and it should be continued until a pressure of about  $10^{-5}$  mm is maintained for

several hours when the system is closed off from the pumps.

The temperature for outgassing depends upon the particular adsorbate and adsorbent under study but it should be as high as possible without causing chemical decomposition of the adsorbent or change of its surface area. No general statement can be made in this regard, the cleaning of a given surface necessarily depends on the way in which the surface is prepared, and upon the particular adsorption process of experimental interest. In general, one can say this, the more care taken in the initial preparation of the adsorbent surface the easier is its subsequent handling. Apart from this, the higher the initial outgassing temperature, provided that one does not change the basic nature of the experimental surface, the more free will the surface be from the chance of the contamination.

*Pressure Measurement.* The measurement of physical adsorption of gases does not usually require attaining pressures less than  $10^{-7}$  mm. Modern mercury or oil-diffusion pumps, when backed by a standard rotary vacuum pump, suffice to produce vacuum of that order. Higher vacuum can be produced by special techniques, but are not considered here. It is, of course, essential to provide suitable cold traps between the pumps and the experimental section of the vacuum line, and also to provide pressure gauges suited to the experimental range of pressures.

Only the best high vacuum greaseless stopcocks should be used. If utterly unavoidable the lubricant should be rightly chosen having a negligible vapour pressure and applied correctly. When employing mercury cut offs in special cases, a very high purity mercury should be used since this is very important in those cases where a measurement depends upon the position of a mercury meniscus.

Various pressure measuring devices used depend upon the type of apparatus and the range of pressures needed. For example, the membrane micrometer can read pressures up to  $10^{-4}$  torr. The McLeod type compression manometer or the heat-conductivity type Pirani gauges can be used up to  $10^{-5}$  torr. Between  $10^{-2}$  and  $10^{-6}$  torr is, therefore, also the Penning gauge needed. For ultra high vacuum measurements (UHV) the ionization gauge can be used which, with

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the help of modulating method, can measure pressures from  $10^{-10}$  to  $10^{-12}$  torr.

With the exception of the membrane and compression manometers the readings of the manometers are generally dependent upon the gaseous species since they function on the principle of heat-conductivity or the ionization of the given gas. Therefore, it is always necessary to calibrate these manometers against the compression manometer. If the gas composition is unknown, as is common in the case of residual gas, the measurement of the pressure could have a serious error.

Due to these reasons, nowadays, for the measurement of low pressures, one needs pressure gauges which allow the measurement of partial pressures. If the pressure is more than  $10^{-6}$  torr, one could use a mass spectrometer possessing a resolving power and sensitivity which suits the given problem. If the partial pressure lies below  $10^{-5}$  torr, one should use an instrument which is specially suitable for ultra high vacuum techniques.

**Volumetric Methods.** The volumetric approach was widely used in early studies of adsorption principally because volumetric methods had been widely developed and applied through the nineteenth century. As an available technique, it was applied to the study of adsorption.

Workers using this technique recognized two basic limitations. The accurate determination of the amount adsorbed demands estimation of the dead space, i.e., the adsorption, particularly important where physical adsorption is concerned, on the parts of the apparatus other than the adsorbent surface. (ii) The need to use finely divided solids in order to yield detectable changes in the external system.

This type of technique has been refined by many workers committed to the study of adsorption upon finely divided solids—a matter of considerable technological importance. There are, however, limitations to the technique, measurement of the quantity of unadsorbed gas is often complicated by the fact that part of the dead space is at room temperature. In addition, there are limitations due to the pressure changes, that are produced in a typical volumetric adsorption experiment for high capacity adsorbent and a low surface adsorbent. It is necessary that, for a low area adsorbent, initial pressures should be in the micron level and the millimeters of mercury level. To allow adsorption on the glass walls of the adsorption cell, it is advisable to measure the surface area of the cell walls and adsorption due to this in 'blank' experiments.

Some specialized volumetric apparatus have been described in literature.<sup>1,2</sup> For example, a low-pressure and low-area adsorption apparatus was designed by Wooten and Brown<sup>3</sup> for which they suggested the use of ethylene or ethane vapours as the adsorbates at liquid oxygen temperature. McLeod gauge has been used for pressure measurements and the mercury cut offs because of the hydrocarbon vapours. To study the adsorption isotherms at very low relative pressures and small surface areas using ethane. Lauterbach *et al.*<sup>4</sup> have used the apparatus shown in Figure 1. Its salient features are the mercury cut offs and a gold-leaf trap protecting the uranium

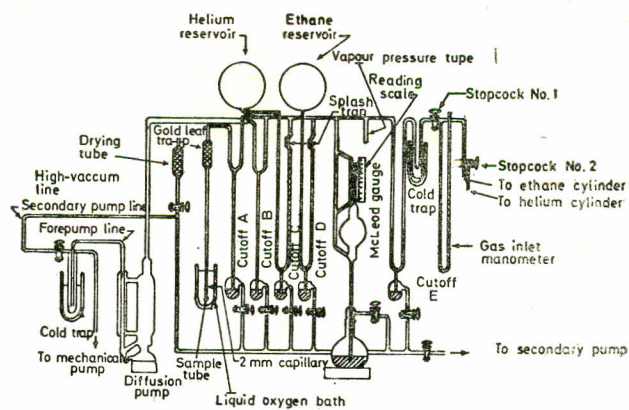


Fig. 1

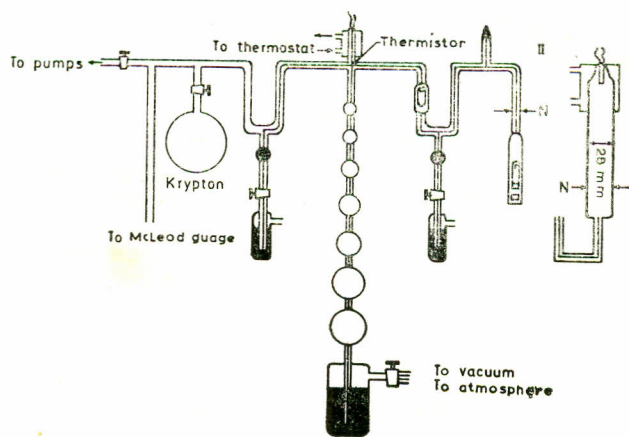


Fig. 2

oxide adsorbent from mercury vapour. Pressures were measured by means of a McLeod gauge and it was possible to use adsorbents of a total surface area of  $1000\text{--}2000\text{ cm}^2$ .

A precise apparatus for the study of adsorption on low specific area surfaces and for  $5\text{--}760\text{ mm}$  pressures is described by Constabaris, Singleton and Halsey.<sup>5</sup> They used a low-temperature adiabatic calorimeter as sample cryostat and precise techniques of gas thermometry for pressure measurements. The cryostat was able to hold a temperature better than  $0.01^\circ$  for extended periods between room temperature and a little below the boiling point of nitrogen.

To measure the adsorption of krypton on freshly created surfaces of germanium Rosenberg<sup>6</sup> used the apparatus shown in Figure 2. Thermistors were used to reduce leakage from the outside atmosphere. Typical surface area of the samples used was as small as  $50\text{ cm}^2$ .

Numerous other methods have been described in the literature but they are not in the scope of the present review. To sum up, it must be mentioned that while volumetric techniques can still play an important role when studying cases of chemisorption, their application to physical adsorption phenomena would appear to be extremely limited. Apart from the difficulties inherent in these techniques there is the problem that at high relative pressures, condensation takes place within the adsorbent grains. This leads

to hysteresis, and makes difficult the study of the high pressure region, a region which is assuming considerable importance.

**Gravimetric Methods.** Basically, gravimetric methods differ from the volumetric techniques in as much as the mass adsorbed is determined directly, avoiding the problem of adsorption upon other parts of the apparatus.

Perhaps the simplest gravimetric techniques are those described by McBain and Bakr,<sup>7</sup> Bushuk and Winkler<sup>8</sup> and by Rhodin.<sup>9</sup> McBain and Bakr simply usually placed finely divided adsorbent in a light bucket suspended from a quartz spring. There is an obvious limitation to the sensitivity of this method. This was further developed by Bushuk and Winkler. Their apparatus consists of a glass beam pivoted on a fine quartz thread. A weighed sample of the solid is suspended from one end of the glass beam and balanced by means of a calibrated quartz spring at the other end. The whole assembly is encased in glass, connected to the vacuum system and immersed in a thermostat. The extension of the spring after the introduction of vapours determines the mass adsorbed at a certain pressure.

Rhodin used a vacuum microbalance shown in Fig. 3, which is one of the most advanced instruments of its kind. Indeed, he classified suitable microbalances under four headings, (a) the cantilever, (b) knife-edge, (c) torsion and (d) the spring types. The maximum sensitivity of the knife-edge type was assessed as  $10^{-6}$  g, the other three types appeared to have a maximum sensitivity of  $10^{-8}$  g. These limits have, and could, be extended. For example, Barret and his coworkers<sup>10</sup> have constructed a torsion microbalance having a sensitivity of  $10^{-9}$  g.

The Cahn balance<sup>11</sup> is commonly used nowadays for adsorption studies. It is an automatic recording device in which the deflection of the balance arm deflects a beam of light and by means of photocells and electronic amplification the current in a solenoid is altered so as to restore the beam to its null position. The sensitivity of a Cahn RG type could be increased

to  $10^{-7}$  g with a smaller load which, in turn, decreases the surface area of the sample. Care must be taken to avoid condensation of liquids on the balance beam. The balance is particularly valuable for the determinations of the rate of adsorption. The Sartorius electronic microbalance has been used<sup>12</sup> for the measurement of the adsorption of nitrogen and krypton on solids having areas as low as  $200 \text{ cm}^2$ .

One major problem with these techniques is the minimization of, and the correction for buoyancy effects. For this purpose, it is desirable to have the adsorbent and counterweight of identical material, matched in weight to  $10^{-5}$  g and immersed to the same depth in identical thermostat baths. Although this matter has received considerable attention, it is bound to become more important in view, the higher sensitivity.

The points of preference for adsorption studies on single, homogeneous and polished crystals, free from pores, crevices and other surface imperfections, over the powdered or highly porous adsorbents of high specific area are self-evident, as the data obtained on the latter surfaces are complicated by heterogeneity effects, the capillary and intergranular condensation, causing hysteresis. With crystal surfaces, it is not only possible to give a definite interpretation of the data in terms of microscopic models, but also derive useful information, through comparative studies, about the nature of the surface heterogeneity and mechanism of capillary adsorption (condensation). However, working with low-specific area is not amenable to the conventional techniques because of the extremely high sensitivity required to determine the amount of adsorbate on limited single crystal substrate. Such investigations can, with proper care, be carried out piezogravimetrically, an indirect gravimetric technique where adsorbed mass of the order of  $10^{-10} \text{ g cm}^{-2}$  or even less can be measured, it is especially suited to adsorbates of very low pressures. It was developed by Slutsky and Wade<sup>13</sup> on the suggestion of Sauerbrey<sup>1</sup> and takes the advantage of the fact that the resonance frequency of a quartz crystal alters with the

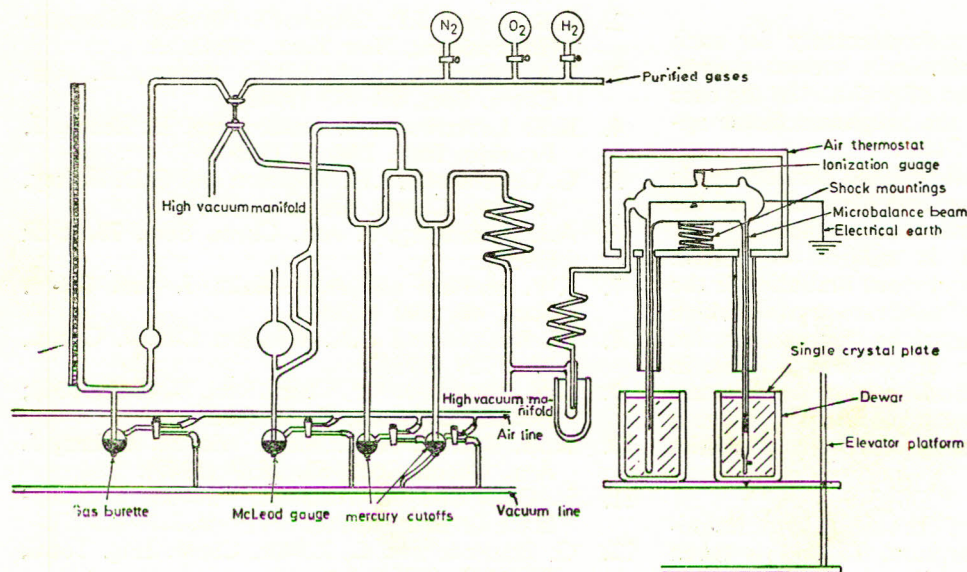


Fig. 3. Vacuum microbalance assembly.

change in the mass of the crystal. Using this approach, they were able to detect mass changes, i.e. amount adsorbed, of the order of  $10^{-8} \text{g cm}^{-2}$  on a quartz crystal having a total area of approximately  $1.5 \text{cm}^2$ . Later, it was used by Bazhanova and Savel'eva<sup>15</sup> for the study of the adsorption of argon and water on single quartz crystal surface.

Khan<sup>16</sup> has used this technique extensively for studying the adsorption of argon, water, n-alkanes, alkylchlorosilanes and alcohols on quartz crystal surfaces. His experimental arrangement is simple and is shown in Fig. 4. The system was largely made of glass and fitted with greaseless stopcocks. Compress-o-coupling tube-fittings were used to connect the adsorbate bulb and the experimental cell. The cell was constructed from stainless-steel, with two kovar-glass seals soldered in the top to ensure a leakage proof connection between the oscillator leads and the electrodes inside. To ensure firm clamping of the crystal, a small pressure differential was maintained through a spring.

A major problem in using this technique consists of estimating reliable corrections for the effects other than those of adsorption, since their magnitude is critical to the reliability of the piezogravimetric method for precision studies of adsorption. The overall contribution of these effects to the resonant frequency for crystals other than AT-cut are quite appreciable and therefore, the technique is not of general applicability. However, of the other techniques available, it appears to be a very suitable one for the following reasons:

(1) In principle, mass changes of the order of  $10^{-9} \text{g cm}^{-2}$  can be determined if sufficient care is taken.

(2) With this sensitivity, geometric or apparent, areas of the order of  $1 \text{cm}^2$  can be used for the experimental adsorbent surface.

(3) Quartz, as a high energy surface, can chemisorb many species. For example, metal films can be evaporated on to them and, as shown by Kington,<sup>17</sup> the technique may be used to determine the thickness of the chemisorbed film.

(4) That the quartz crystals necessary for such studies are now readily available in various shapes, sizes, crystal cuts and degrees of polish. In the case of very well-polished discs, the roughness factor appears to be of the order of two.

(5) The use of small, well-polished surfaces tends to reduce uncertainties arising from hysteresis, and the heterogeneity shown by most solid surfaces.

Piezogravimetric method is subject to certain limitations, of course. One obvious limitation is the comparatively small range of substrate crystals which can be used. The crystal must be piezoelectric, i.e. must not possess a centre of symmetry. This, in turn, leads to a limitation on the upper temperature at which the crystal may be operated since, above a critical temperature, the piezoelectric characteristics are destroyed.

As a general comparison of the suitability of techniques for the study of adsorption, Table 1 is taken from the article by Reucroft<sup>18</sup>.

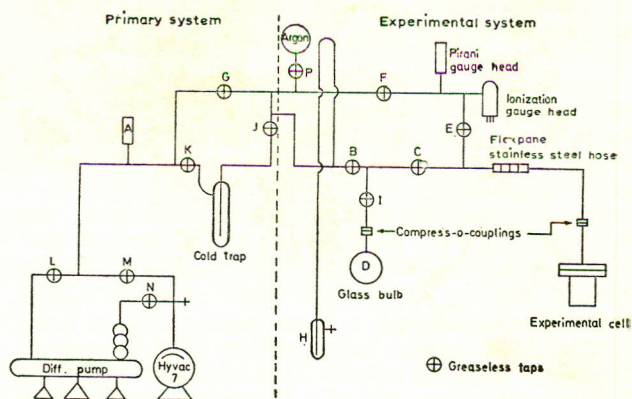


Fig. 4.

TABLE 1. COMPARISON OF ADSORPTION TECHNIQUES.

Surface area of sample (sq. cm <sup>2</sup> )	Suitable adsorption technique
1000-2000	Volumetric (conventional)
50-400	Volumetric (special)
< 50	Vacuum microbalances
< 10	Piezogravimetric

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### References

- D.M. Young and A.D. Crowell, *Physical Adsorption of Gases* (Butterworths, London, 1962).
- S. Ross and J.P., Olivier, *On Physical Adsorption* (Interscience, New York, 1964).
- L.A. Wooten, and J.R.C. Brown, *J. Am. Chem. Soc.*, **65**, 113 (1943).
- K.E. Lauterbach, S. Lasken and L. Leach, *J. Franklin Inst.*, **250**, 13 (1950).
- G. Constabaris, J.H. Singleton and G.D. Halsey, *J. Phys. Chem.*, **63**, 1350 (1959).
- A.J. Rosenberg, *J. Am. Chem. Soc.*, **78**, 2929 (1956).
- J.W. McBain and A.M. Bakr, *J. Am. Chem. Soc.*, **48**, 690 (1926).
- W. Bushuk and C.A. Winkler, *Can. J. Chem.*, **33**, 1729 (1955).
- T.N. Rhodin, *J. Am. Chem. Soc.*, **72**, 4343 (1950); *Advan. Catalysis*, **5**, 39 (1953).
- H.M. Barrett, A.W. Birnie and M. Cohen, *J. Am. Chem. Soc.*, **62**, 2839 (1940).
- L. Cahn and H.R. Schutz, *Vacuum Microbalance Techniques*, Plenum Press, **3**, 39 (1962).
- G. Sanstede and E. Roster, *Chem. Eng. Tech.*, **32**, 413 (1960).

13. L.J. Slutsky and W.H. Wade, *J. Chem. Phys.*, **36**, 2688 (1962); *J. Chem. Phys.*, **40**, 3394 (1964).
14. G. Sauerbrey, *Z. Physik.*, **155**, 206 (1959).
15. E.A. Bazhanova and Z.I. Savel'eva, *Sov. J. Phys. Chem.*, **43**, 907 (1969).
16. G.M. Khan, *Rev. Sci. Instr.*, **43**, 117 (1972).
17. B.W. Kington, *Marconi Instrumen.*, **10**, 81.
18. P.J. Reucroft, *Conference of Surface Effects in Detection*, 197 (1964).