A Simple Method for Comparing the Shapes of Closely Related Adsorption Isotherms

By S. John Gregg

(*School of Chemistry, Brunel University, Uxbridge* UB8 3PH)

Summary The divergence of the adsorption isotherm of an experimental solid from that of a reference sample is readily shown up by calculating the ratio, *f*, of the ordinates of the two isotherms at a series of values of relative pressure P/P°, and plotting *f* against P/P°.

When using the adsorption of vapours for the study of the texture (the surface area and porosity) of active solids, one often encounters the problem of deciding whether or not the shape of the isotherm within a series of related samples has changed with treatment, method of preparation, *etc.* The well-known *t*-plot,[1] and more recently the α_s-plot,[2] have already proved their value in this context, but their application involves the sometimes difficult decision as to whether a plot has or has not deviated from strict linearity.

An alternative device for the comparison of the shape of the isotherm of a given sample with that of a reference sample is to read off the ordinates of the two isotherms at intervals (say 0·05 or 0·1) of relative pressure P/P°, calculate the value of their ratio, *f*, say, at each value of P/P°, and plot *f* against P/P°. Changes in the shape of the isotherm of the given solid from that of the reference sample show up clearly as deviations of the f-plot from the horizontal.

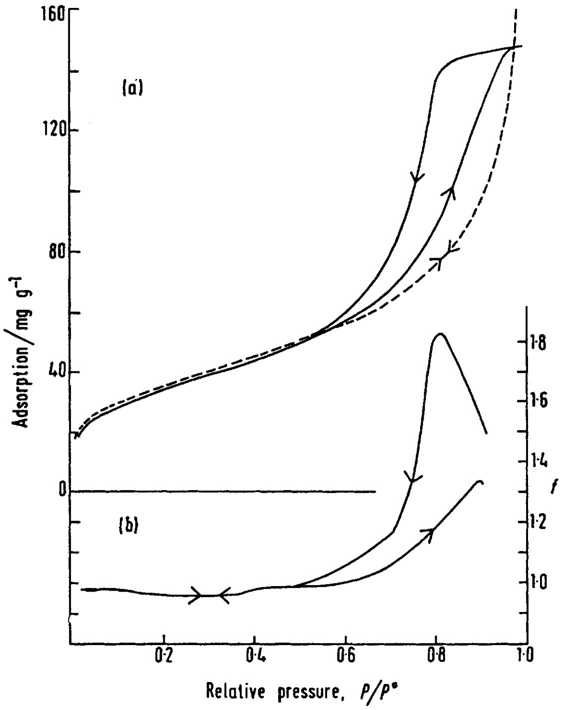

Figure 1. Adsorption of nitrogen at 77 K on an alumina powder: (a) adsorption isotherms, (b) f-plot. Broken line, uncompacted powder; continuous line, powder compacted at 1·48 × 10^9 N/m^2 (96 ton/in^2). —>— adsorption; —<— desorption.

The method is illustrated by reference to two powders, one of alumina and one of silica, in the form of spherical particles prepared by a flame method; the primary object[3] was to find the effect of compaction on the surface area and porosity of each sample, by a study of the adsorption of nitrogen at 77 K. The uncompacted powders gave isotherms of Type II (Figures 1a and 2a dotted lines), characteristic of monolayer–multilayer adsorption on an 'open' surface. After the samples had been compacted in a die at high pressure, the isotherms assumed the type IV shape characteristic of adsorption on a porous solid, because of the production of pores (the interstices between closely packed particles).

A question of particular interest is whether the process corresponding to the adsorption branch of the hysteresis loop was capillary condensation or multilayer formation. As is seen from Figure 1b, the f-plot for alumina displays a marked rise in the region corresponding to the adsorption branch of the loop, indicating that capillary condensation is occurring; for silica, on the other hand, the f-plot is almost horizontal in this region (Figure 2b), so that the predominant process is still multilayer formation, just as on the open surface of the uncompacted material. For the desorption direction, the f-plots of both substances show, as expected, the positive deviation indicative of capillary condensation. It is probable that the changeover from multilayer formation to capillary condensation in the case of the silica occurs when $P/P^\circ \rightarrow 1$; desorption can then take place through capillary evaporation by a Kelvin-type mechanism.

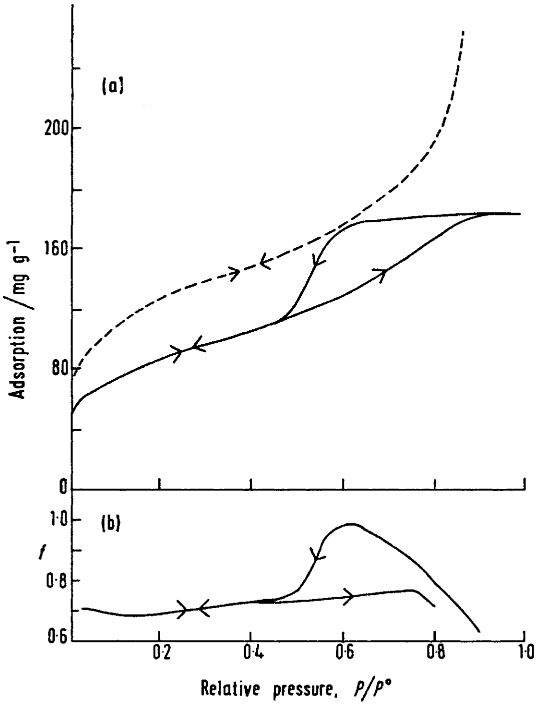

Figure 2. Adsorption of nitrogen at 77 K on a silica powder: (a) adsorption isotherms, (b) f-plot. Broken line, uncompacted powder; continuous line, powder compacted at 2·00 × 10^9 N/m^2 (130 ton/in^2). —>— adsorption; —<— desorption.

Possible reasons for this rather striking difference in the behaviour of the two systems, which could scarcely have been suspected from mere inspection of the isotherms themselves, together with an account of similar work on a number of other powders with different characteristics, will be presented elsewhere.

(*Received*, 25*th June* 1975; *Com.* 719.)

---

[1] B. C. Lippens and J. H. de Boer, *J. Catalysis*, 155, **4**, 319.

[2] K. S. W. Sing, *Chem. and Ind.*, 1968, 1520; 'Surface Area Determination,' eds. D. H. Everett and R. H. Ottewill, Butterworths, London, 1970, **25**.

[3] J. F. Langford, Ph.D. Thesis, Exeter University, 1967.

Printed by Heffers Printers Ltd Cambridge England