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A simple apparatus for measurement of adsorption of gases from low to high pressures

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Abstract. A simple, relatively precise apparatus which permits absorption measurements to be made at pressures from about 10 torr to about 40 atm is described. It involves the use of a transducer or a pressure cell. The use of a transducer, because of its small internal volume and the accuracy with which its output can be read potentiometrically, gives this apparatus an advantage over one in which pressures are measured by a conventional Bourdon-tube gauge. When surface areas of about 50 m^2 are to be measured, about 120 cm^3 s.t.p. of a gas such as xenon or carbon dioxide are required and the surface areas (calculated from the equation of Branauer, Emmett and Teller) are capable of duplication to within $\pm 2\%$.

The apparatus, made of stainless steel, is shown diagrammatically in the figure. It was made to order, following the authors' design, by Tem-Pres Research, Inc. The transducer T (Statham Instruments, Inc., model No. PA 731–TC–500–350) is connected by means of stainless-steel capillary tubing (inside diameter 17 thou) to valves $V_1V_2V_3$ (Aminco High Pressure, 30000 lb in^{-2}) through the intermediary of an Aminco super-pressure cross C.

The sample tube S (2–3 cm^3 capacity in the present case, but it may be modified to suit the requirements of the investigation) is detachable and is secured by means of a cone seating to a $\frac{1}{4}$ in., $\frac{9}{16}$ in. Aminco adapter which in turn is connected to valve V_1. The dead space of the connecting tubes between (i) the Aminco adapter and valve V_1 and (ii) between the transducer and the super-pressure cross C is minimized by insertion of proper stainless-steel rods.

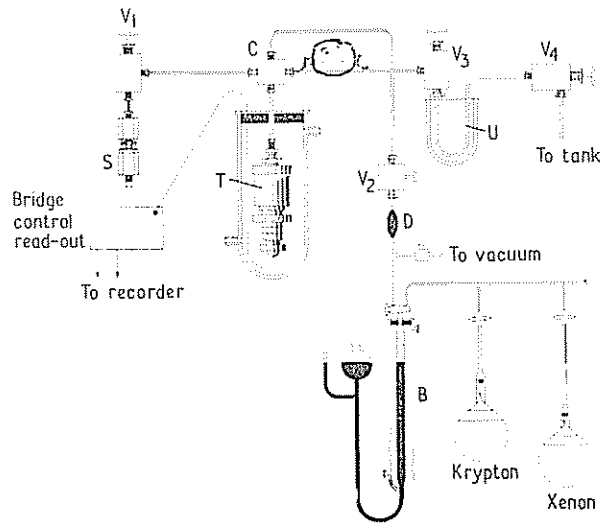
The stainless-steel capillary tubing is connected to the valves through small lengths (not shown in the figure) of $\frac{1}{4}$ in. outside diameter stainless-steel tubing threaded and tapered to a cone. The coupling is brought about by a gland nut and an inner sleeve. Silver soldering is employed throughout.

Gas cylinders can be connected to the condensing coil U (of $\frac{1}{4}$ in. inside diameter stainless-steel tubing) at V_4. Gases such as krypton and xenon are connected to the apparatus at D by a seal of Cenco high vacuum tape and Fischer's Sealit compound.

The output from the transducer is measured on a bridge control read-out instrument (Statham Instruments model BCR1–0) coupled to a recorder. Since the transducer does not have a negligible temperature coefficient, it is enclosed in a jacket through which water at a temperature of $28 \pm 0{\cdot}1$°C is circulated by means of a Tecam Tempunit (Lapine Instrument Co.). It is advisable to circulate the water for at least two hours prior to an adsorption run so that temperature equilibrium is closely attained.

The transducer is calibrated using a suitable hydrocarbon vapour (propane) as standard. The vapour is condensed in the cooling coil U by surrounding the latter with a Dewar of liquid nitrogen. The condensate is then evaporated into the sample tube whose temperature is varied between 0°C and room temperature. The temperature and the corresponding transducer output are noted and, from the known vapour pressure–temperature relationship of the hydrocarbon, the calibration curve of the transducer is obtained.

The calibration of the apparatus and the procedure for making an adsorption run are as described previously



Diagrammatic view of high pressure adsorption apparatus.

(Kini 1964). The calibrations are reproducible to within $\pm 0{\cdot}5\%$. The sample volume is determined by helium displacement at 200°C (Kini and Stacy 1963).

An isotherm was first determined for adsorption of nitrogen at 77°K on Graphon, a graphitized carbon black having a highly homogeneous surface (Walker 1962). Using the BET equation (Brunauer, Emmett and Teller 1938) an area of 90 ± 1 $m^2 g^{-1}$ was calculated. This agrees well with the area of $89{\cdot}7$ $m^2 g^{-1}$ (the value supplied by Cabot Corp., Cambridge, Mass.) obtained from adsorption measurements of nitrogen at 77°K, using a conventional low pressure volumetric gas adsorption apparatus (Emmett 1941).

This apparatus has been particularly useful in measuring surface areas of molecular sieve materials (Kini 1964). Because of possible activated diffusion of the adsorbate, it is essential that the adsorption be conducted at the highest

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practical temperature so that essentially all of the solid surface area is reached by the adsorbate in a reasonable equilibration time; but to use the BET equation to calculate accurately surface areas from adsorption isotherms, it is necessary to have adsorption data up to a relative pressure of about 0·2. Thus, if adsorption is to be conducted at temperatures higher than usual, an apparatus capable of operating at higher pressures must be available so that the required relative pressures can be obtained. Particularly suitable adsorption conditions for estimating most closely the total surface area of molecular sieve materials appear to be carbon dioxide as the adsorbate at 25°c (Walker and Kini 1965). The critical temperature of carbon dioxide is 31·1°c and the vapour pressure at 25°c is 63·5 atm. Under these conditions surface areas can be duplicated within ±2% provided a sample of at least 50 m^2, total area, is available for the measurement.

A special mention is to be made of the Linde molecular sieve 4A. This material exhibits a surface area of less than 10 m^2g^{-1} by the usual BET method, which employs the adsorption of nitrogen at liquid nitrogen temperature. When measured by the adsorption of CO_2 at 25°c, values above 300 m^2g^{-1} are obtained for a material degassed at about 200°c (the values for this material are highly dependent upon the temperature of degassing).

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References

BRUNAUER, S., EMMETT, P. H., and TELLER, E., 1938, *J. Amer. Chem. Soc.*, **60**, 309–19.

EMMETT, P. H., 1941, *A.S.T.M. Technical Publication*, **51**, 95–105.

KINI, K. A., and STACY, W. O., 1963, *Carbon*, **1**, 17–24.

KINI, K. A., 1964, *Fuel, Lond.*, **43**, 173–80.

WALKER, P. L., JR., and KINI, K. A., 1965, *Fuel, Lond.*, in the press.

WALKER, P. L., JR., 1962, *Amer. Scient.* **50**, 259–93.

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