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MEASUREMENT OF LOW SURFACE AREAS, OF UO$_2$ PELLETS, BY THE KRYPTON GAS-ADSORPTION METHOD

by

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INTRODUCTION

Of the various techniques available (1) for surface-area measurements, methods based on the physical adsorption of gases (such as nitrogen, krypton or xenon) on solids, at liquid nitrogen temperature, are generally considered to be the most reliable. The specific surface areas of solids may be calculated from the gas-adsorption data using the standard adsorption isotherms of Brunauer, Emmet and Teller (2) (B.E.T.) or of Harkins and Jura (3). If 'P' refers to the equilibrium adsorption pressure of the gas and 'P_o' refers to the saturation vapour pressure of the same gas in the condensed liquid state, the B.E.T. plots are linear in the P/P_o range of 0.05 to 0.35 for nitrogen (2) and of 0.07 to 0.2 for

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krypton (4,5), and hence applicable for surface-area calculations in this range. At liquid nitrogen temperatures, the P_O value for krypton is only 2-3 mm Hg compared to the high P_O value ($\sim$1 atmos) of nitrogen. Hence, as a rule, nitrogen is not used for determining low surface areas because small changes in the high values of P_{N_2}, during adsorption, cannot be measured accurately. The use of gas chromatograghic techniques (6-8), using a continuous gas flow and a pressure-recording system, has, however, improved the speed as well as the sensitivity of the nitrogen gas-adsorption method. These chromatographic techniques have extended the lower limit of surface-area measurement to about 1000 cm^2/g, using a 5-g sample. However, the use of samples larger than 5 g has been found to cause thermal diffusion streams which result in an erratic pressure response. Equipment based on the above principles is now commercially available from a number of companies (e.g. Perkin-Elmer Corporation, Norwalk, U.S.A., Sorptometer, Model 212-D).

Krypton can be used in measuring small as well as moderately large surface areas by gas-adsorption methods. However, a limitation in using krypton for measuring large surface areas is that very small quantities of sample (a few mg for a sample of several m^2/g in area), which may not be representative of the bulk material, would have to be used. Xenon has been used (9-12) exclusively for measuring very low surface areas (a few cm^2). There is, however, considerable

uncertainty (11) concerning the cross-sectional area of a xenon molecule. Hence, for surface-area measurements, one has to make a judicious choice of the method to be used, depending on several factors; e.g. the nature and amount of material available, its apparent surface area and surface roughness, and the experimental accuracy required.

This report describes techniques developed in this laboratory for measuring the individual surface area (total surface area $\sim$100 cm^2) of UO_2 pellets that were sent to us for surface-area measurement by the Nuclear Research Laboratories, Chalk River, Ontario. Each pellet had a geometrical surface area of 13.1 cm^2 and a volume of 3.65 cm^3. This is a typically difficult case for precise surface-area measurements because of the large ratio of dead space (that would be occupied by the pellet) to surface area involved. It is evident from the pellet dimensions that compared to the surface area of the pellet, the surface area of the glass walls of the adsorption bulb (and of the connecting tube) would be considerable. Hence, the surface area of the adsorption bulb and of the tubing has to be determined separately (blank), and then subtracted from the total measured surface area of the pellet and that of the glass walls. This difficulty becomes more serious if the volume of gas in the dead space is not much less than the volume of gas adsorbed on the container walls, when even small errors in dead-space determinations would result in large errors in surface areas.

The techniques used to overcome the above difficulties in measuring the surface areas of the UO_2 pellets, within 5% experimental error, will be described in the following sections. The apparatus used and the details of the B.E.T. method of determining surface areas using krypton gas have been described in a previous Mines Branch Bulletin (13).

EXPERIMENTAL

Except where mentioned, the experimental method and the procedure for calculating the surface area were the same as described earlier (13). However, the apparatus used for the gas-adsorption studies is shown in Figure 1 for reference. The characteristics of the thermistor gauge used for measuring the gas pressure had changed (2-3%) after about three years of use. Hence, the thermistor was recalibrated for measuring the absolute pressures of helium and krypton using a McLeod gauge. The gas-storage bulbs were freshly filled with research-grade (99.99%) krypton and helium from their respective gas cylinders. The glass adsorption bulbs were made as symmetrical as possible and were just wide enough to accommodate the UO_2 pellets. These bulbs, containing the UO_2 pellets, were sealed to the apparatus leaving 0.5 cm space above the pellet in order to avoid excessive heating of the UO_2 pellet while the glass was sealed.

Measurement of Dead Space and the Krypton Adsorption

The four adsorption bulbs (Figure 1) containing the UO_2 pellets were evacuated overnight while the samples were heated simultaneously at 100°C by means of electrically heated sand baths. The dead space was determined using helium. The adsorption of krypton on the UO_2 pellets was measured to obtain 3-4 points in the lower permissible range of P/P_o (0.07-0.2 used in B.E.T. equation) where the pressure measurements are more sensitive than in the upper range. The adsorption bulbs (I-IV) of the gas burette were filled with mercury and only the remaining, small, calibrated portion (V_c = volume between G and the stopcocks 2, 5, 10, 11, 12 and 13 in Figure 1) was used in the gas-adsorption and dead-space measurements. Under these conditions, the relative decrease in gas pressure during adsorption and during dead-space determinations is much larger than when the entire gas burette is used. This procedure increases the sensitivity of the pressure measurement and reduces the experimental error.

Correction for Krypton Adsorbed on the Glass Walls

Because of the large ratio of dead space to surface area (of glass walls) for the empty adsorption bulb, the error in measuring the dead space was found to be considerable when compared to the amount of krypton adsorbed on the glass walls. As a result, the surface area of the empty adsorption bulb

could not be measured directly with sufficient accuracy. This
difficulty was overcome by filling the adsorption bulb with
fire polished, Pyrex-glass rods of known dimensions. This
procedure of filling the adsorption bulb with glass rods helped
in reducing the dead space while the surface area was increased
at the same time. The adsorption bulb containing the glass rods
was evacuated as before at 100°C and this was followed by the
dead-space and the surface-area measurements.

RESULTS AND DISCUSSION

Figure 2 shows the B.E.T. plots for the adsorption of
krypton on different UO_2 pellets including the gas adsorbed on
the glass walls. The B.E.T. plot for krypton adsorbed on the
surfaces of the adsorption bulb and the glass rods is also shown
in Figure 2. The experimental surface area of the glass bulb
plus the glass rods as calculated from the B.E.T. plot was
81 cm^2, compared to the measured, geometrical surface area of
the adsorption bulb and glass rods of 85 cm^2. Thus the experi-
mental roughness factor for the fire polished glass is close to
unity within 5% error. The small difference in the calculated
and measured surface areas is partly due to the experimental
error in adsorption measurements and partly due to the error in
measuring the geometrical surface area of some geometrically
unsymmetrical portions of the connecting glass tube.

Therefore, the actual surface area of each UO_2
pellet was obtained by subtracting the calculated geometrical
surface area of the glass walls (30-32 cm^2) from the experi-
mentally obtained sum of the surface areas of the pellet and
of the glass walls. The corrected surface areas of the four
UO_2 pellets were thus found to be 153, 126, 102 and 80 cm^2.
The reproducibility of the above experiments was checked by
duplicate measurements and the duplicate values were found
to agree within 5% error.

The geometrical surface area of each pellet was
13.1 cm^2, thus giving a roughness factor of 11.7, 9.6, 7.8 and
6.1 for each of the four pellets. Although the density of
these UO_2 pellets was close to the theoretical value, their
surfaces had been prepared by rough machine grinding and
polishing, thereby greatly increasing the surface roughness.
This was confirmed qualitatively by examining the scanning
electron-microphotographs of the pellet surfaces that are
shown in Figure 3. These photographs indicate several crests
and channels so that the roughness factors will obviously be
several times unity. No accurate evaluation of the roughness
factors can be made from these electron microphotographs
because of the uneven distribution of the geometrically
irregular crests and channels. The krypton gas-adsorption
method for determining absolute surface areas is however found
to be quite reliable. The roughness factor for the fire polished
glass-surfaces may be taken as unity within 5% error relative to
the surface area of the glass involved.

ACKNOWLEDGEMENTS

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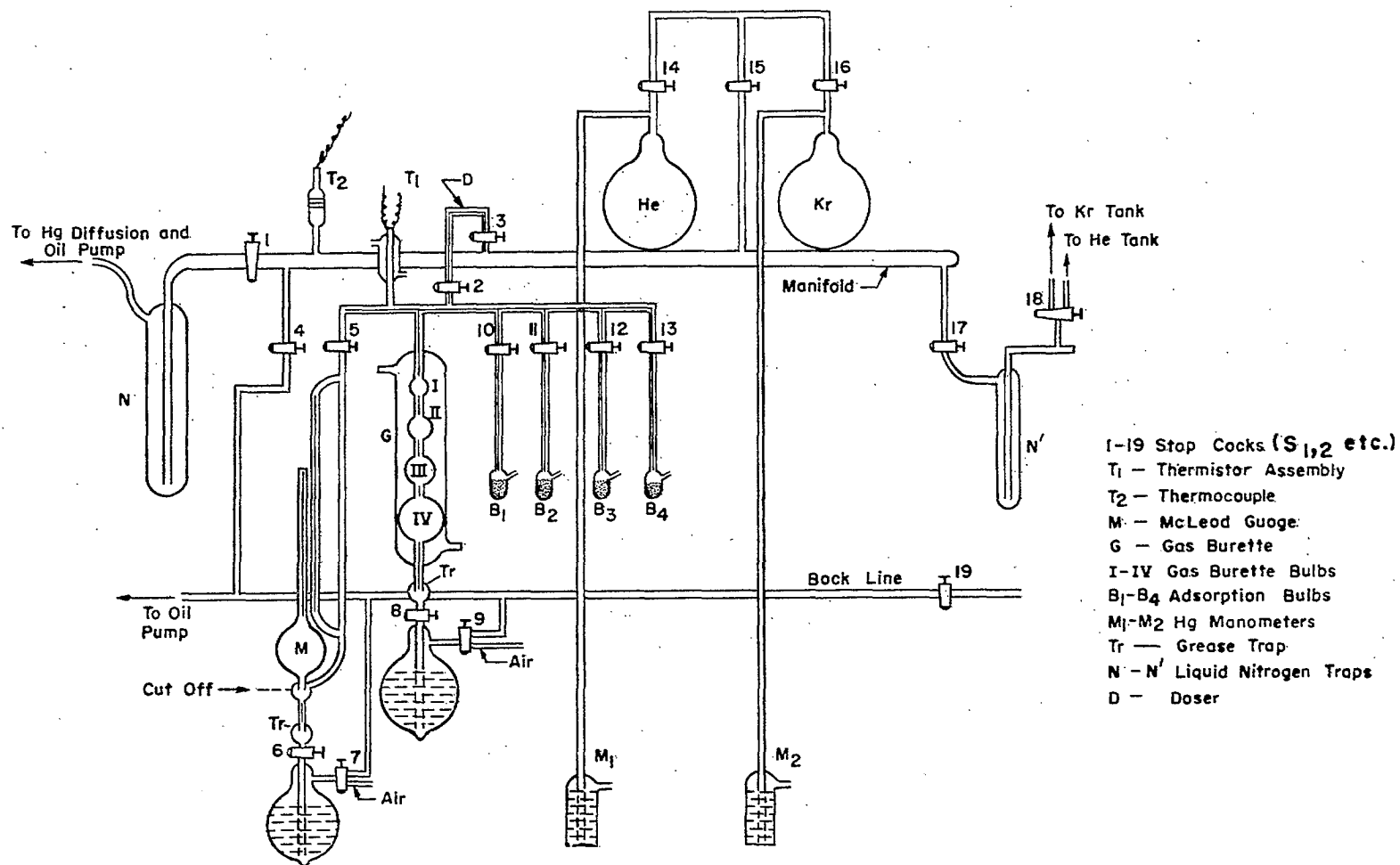   Energy, Mines and Resources, Ottawa (1966).

Figure 1   Apparatus for the Surface-Area Measurements
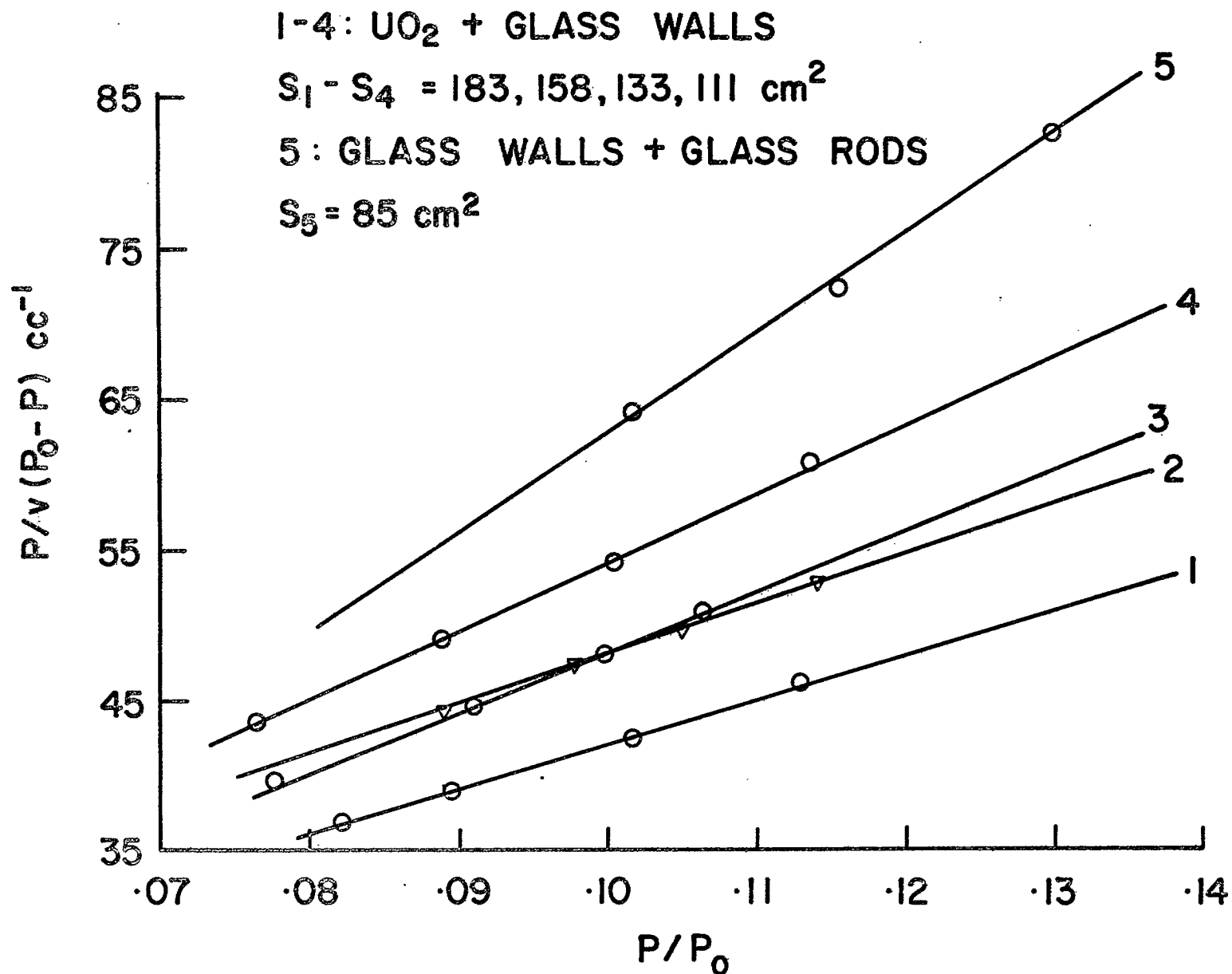by Krypton Gas Adsorption

Figure 2   The B.E.T. Plots for Krypton Gas Adsorption on:
(i) the UO2 Pellets and Glass Walls of Adsorption Bulb;
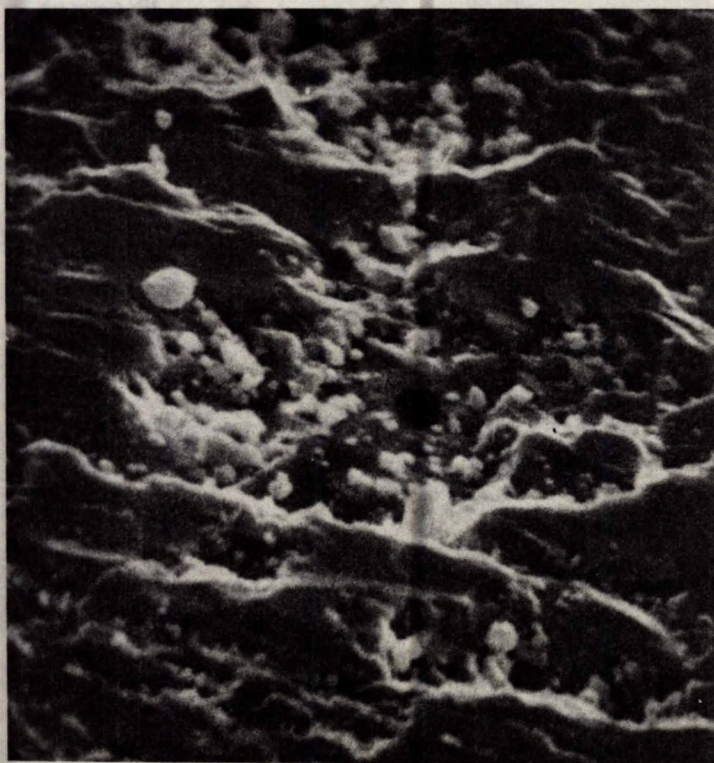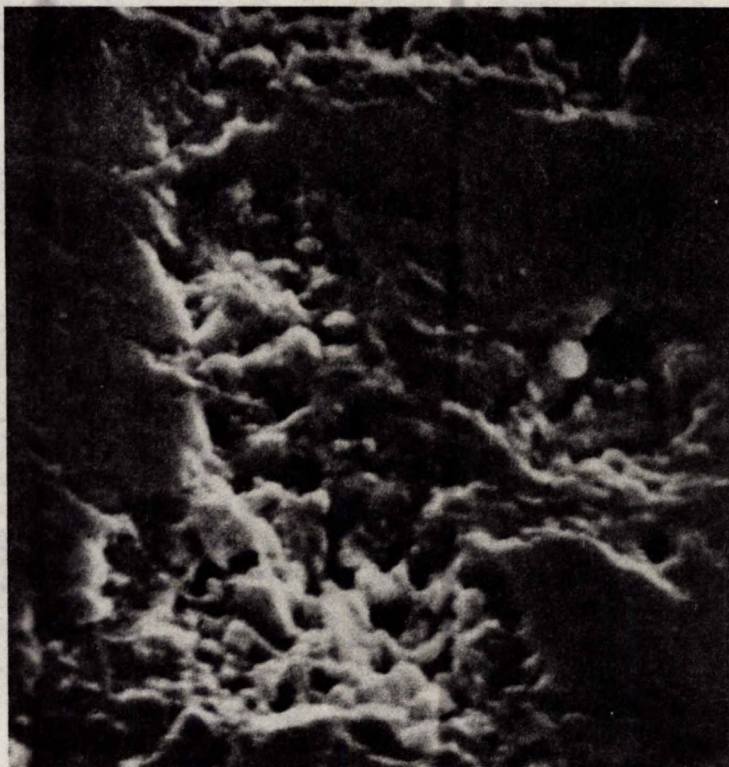(ii) the Walls of Adsorption Bulb and Glass Rods.

Figure 3(a,b)   The Electron Microphotographs of the Surfaces of UO_2 Pellets.   Magnification 6000 X.

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Figure 3(c,d)   The Electron Microphotographs of the Surfaces of UO_2 Pellets. Magnification 6000 X.