surprising because, generally, data measured by dynamic methods are higher than those determined by static methods.

The values for the heat of adsorption and the entropy of lithium chloride salt for the transition from anhydrous to monohydrate were calculated as detailed by Thakker et al. (1967, 1968). The heat of adsorption of LiCl·H<sub>2</sub>O given by Slonim and Huttig as 1465 B.t.u. per pound of water agreed with our calculated value of 1490. The calculated entropy change was 6.361 B.t.u. per pound of water per degree Rankine. The calculated free energy change was 1924 B.t.u. per pound of water.

### Conclusions

The vapor pressures of several hygroscopic salts were measured using the method described. An experimental method for the determination of the transition point for the hydrates has also been established. These and other details are given by Thakker et al. (1968) and Chi (1968).

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### Literature Cited

Chi, C. W., Ph.D. thesis, Illinois Institute of Technology, 1968. Foote, H. W., Foote Mineral Co., Exton, Pa., unpublished data, 1965.

- Gokcen, N. A., J. Am. Chem. Soc. 73, 3789 (1951).
  Slonim, C. H., Huttig, G. F., Z. Physik. Chem. 141, 55 (1929).
  Thakker, M. T., M.S. thesis, Illinois Institute of Technology, 1967.
- Thakker, M. T., Chi, C. W., Peck, R. E., Wasan, D. T., J. Chem. Eng. Data 13, 553 (1968).

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# DETERMINATION OF THE MICROSCOPIC SURFACE AREA **NF** POLYETHYLENE FILM

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An apparatus for measuring the surface area of plastic film by the krypton adsorption method has been developed. The surface area of a polyethylene film was measured and its roughness factor shown to be about unity.

N CONNECTION with the reactions on the surface of polymeric material, we were interested to know the microscopic surface area of a polyethylene film. It is known that the microscopic surface area of solids may be considerably larger than that calculated from their macroscopic dimensions: the ratio of the microscopic to the macroscopic surface is termed the roughness factor. Since polyethylene can be looked upon as a very viscous liquid, the roughness factor was expected to be not much greater than unity. The problem was therefore to determine the microscopic surface area of a substance with a very low specific surface area.

For this purpose Beebe, Beckwith, and Honig have suggested (1945) determining the BET adsorption isotherms with krypton at 78° K. (boiling point of nitrogen). In the usual experimental arrangement the adsorption vessel is connected through a capillary tube with the pressure gage at room temperature. The vessel is immersed up to a mark on the capillary tube in boiling nitrogen. In that case the volumes at 78° K. and room temperature are sufficiently well defined. Such an arrangement is suitable for powders which can be introduced through the capillary tube. As polyethylene film could not be introduced in such a way, it was necessary to use a relatively wide tube to connect the cold and warm sections; this had the further advantage of avoiding pressure drops due to thermal transpiration (Knudsen effect). On the other hand, a special method had to be developed to reduce the uncertainty in defining the cold and warm zones.

### Procedure

The adsorption vessel used (Figure 1) was about 10 mm. in diameter and 150 mm. long; at its upper end it was connected through a conical ground joint to a storage vessel, a vacuum line, and a Pirani vacuum gage. A measured amount of polyethylene film was crumpled and introduced into the lower portion, A, of the adsorption vessel. Adhesion to the wall was avoided by a small number of protrusions.

Two thermocouples, B and C, were glued with epoxy resin to the outer wall above the lower portion of the adsorption vessel, at a vertical distance of 4 mm. from each other. Over the upper thermocouple, C, a heating wire was wound and connected to a variable power source, D. A vacuum flask with liquid nitrogen was jacked up until the surface of the boiling nitrogen reached the upper thermocouple and the current through the heating wire was adjusted until the upper thermocouple showed room temperature. The nitrogen level was kept such that the lower thermocouple indicated the boiling point of nitrogen. The surface, E, bisecting the distance between the two thermocouples was taken as the dividing line between the volume at 78° and 300° K. (thermostated room temperature). The volumes were determined in the usual way by weighing with water.

## Results

Before determining the surface area of polyethylene film, the apparatus was tried out on  $\gamma$ -alumina powder. The sur-