

Essentially similar results were obtained in another experiment.

DEPARTMENT OF CHEMISTRY  
IOWA STATE COLLEGE  
AMES, IOWA

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### Effect of Wetting on the Nitrogen Adsorption-Desorption Isotherm of a Silica Aerogel

BY MARVIN F. L. JOHNSON AND HERMAN E. RIES, JR.

A large pore, high area silica aerogel has been transformed without sintering into a small pore xerogel structure with negligible change in BET area.<sup>1</sup> The silica aerogel was prepared under the supervision of Dr. J. L. Gring of these Laboratories, using the methanol exchange method of Kistler.<sup>2</sup> The small pore xerogel type sample was obtained by immersing the aerogel in water (room temperature, 1.5 hours) followed by drying (110°, 12 hours; 593°, 2 hours).

The two nitrogen adsorption-desorption isotherms (Fig. 1) nearly coincide in the lower relative pressure region indicating similar BET areas: aerogel, 796 sq. m./g.; wetted aerogel (xerogel), 813 sq. m./g. BET plots are good straight lines in the 0.05 to 0.25 relative pressure range for both materials. The aerogel adsorption at  $p_0$  is six times that of the small pore system whose structure is a xerogel type. Pore volumes are thus, respectively, 3.90 cc./g. and 0.66 cc./g. Average pore radius (or platelet separation) calculations<sup>3</sup> from pore volume and BET area show a reduction from 98 to 16 Å. by the treatment. These average radii are in qualitative agreement with Kelvin radii calculated from the steepest portions of the desorption curves; that of the aerogel is also in agreement with electron microscope observations. The desorption isotherms, furthermore, demonstrate narrow pore size distributions for both materials.

Kistler, Fischer and Freeman have suggested a three-dimensional network of needles or filaments as the probable structure of silica aerogels and presumably of xerogels.<sup>4</sup> According to this picture and the adsorption data, drying a wetted aerogel causes shrinkage or the closer packing of the needle-like fibers whose combined surfaces comprise the total catalyst area. Additional observations qualitatively supporting this picture of the structure are: the very low bulk density of the aerogel, 0.14 g./cc.; the increase in density to 0.49 g./cc. on treatment; the extreme fragility of the aerogel compared to the xerogel. Furthermore, the optical microscope shows uniformity in the xerogel structure in agreement with the narrow distribution of pore size.

The above observations indicate that re-exposure of an aerogel to water effects a contrac-

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- (2) Kistler, *J. Phys. Chem.*, **36**, 52 (1932).
- (3) Ries, Johnson and Melik, *J. Phys. Colloid Chem.*, **53**, 638 (1949).
- (4) Kistler, Fischer and Freeman, *THIS JOURNAL*, **65**, 1909 (1943).

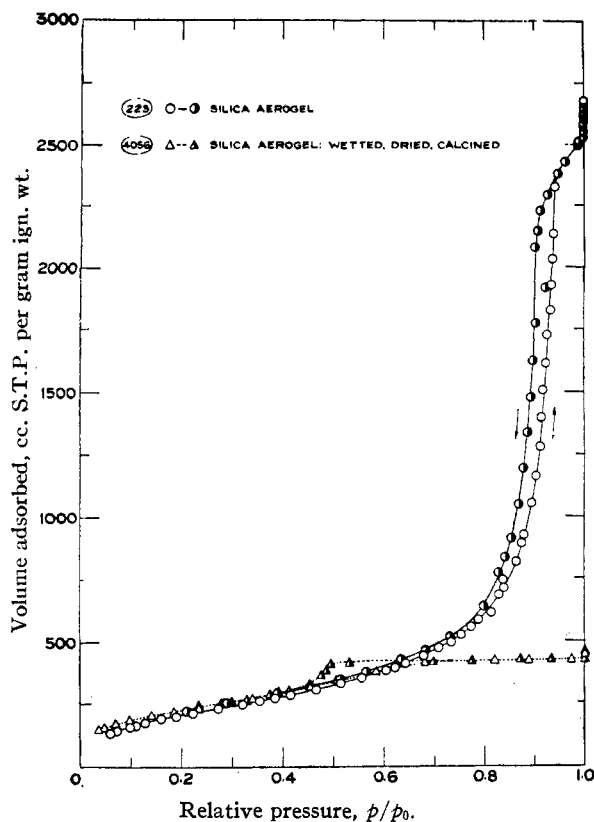


Fig. 1.—Effect of wetting on the nitrogen adsorption-desorption isotherm of a silica aerogel.

tion with no significant change in the surface area. Presumably, the same surface tension forces are operative as those which cause any hydrogel to contract during drying to the xerogel stage. The data appear to support the proposed picture of gel structure.<sup>4</sup> The results also support the applicability of the BET area method to small pore structures since it is generally accepted for large pore systems.

RESEARCH AND DEVELOPMENT DEPARTMENT  
SINCLAIR REFINING COMPANY  
HARVEY, ILLINOIS

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### Inhibition of Trypsin by Cholesteryl Malonic Acids and by *i*-Cholesteryl Acetic Acid

BY EMIL KAISER AND ROBERT HUBATA

The trypsin inhibiting effects of crystalline proteins prepared from pancreas,<sup>1</sup> from soybean meal,<sup>2</sup> and from egg white<sup>3</sup> have been reported. Salts of fatty acids,<sup>4</sup> salts of citric acid,<sup>5</sup> carbonyl

- (1) (a) Northrop, Kunitz and Herriott, "Crystalline Enzymes," Columbia University Press, New York, N. Y., 1948; (b) Kazal, Spicer and Brahinsky, *THIS JOURNAL*, **70**, 3034 (1948).
- (2) (a) Ham and Sanstedt, *J. Biol. Chem.*, **154**, 505 (1944); (b) Bowman, *Proc. Soc. Exp. Biol.*, **57**, 139 (1944); (c) Kunitz, *J. Gen. Physiol.*, **30**, 219 (1947).
- (3) Balls and Swensen, *J. Biol. Chem.*, **106**, 409 (1934).
- (4) Peck, *THIS JOURNAL*, **64**, 487 (1942).
- (5) Pamfil and Maxim, *Klin. Woch.*, **17**, 1651 (1938).