ably about 0.2%. The main difficulty is in estimating the concentration by titration with relatively small quantities of solutions. I wish to express my gratitude to Det videnskapelige forskningsfond and to Universitetets jubileumsfond for grants enabling me to carry out these investigations and toward Norsk Hydro-Elektrisk Kvælstofaktieselskab for placing heavy water at my disposal. I also wish to thank Docent Dr. Frivold and Professor Dr. Hassel for helpful suggestions and for constant interest throughout the progress of this research.

Summary

A vacuum distilling apparatus for deuterium oxide, and a conductivity cell are described. The construction of the cell allowed measurements to be carried out in an atmosphere of hydrogen.

Conductance measurements at 25° are reported on solutions of NaOH in H_2O, and of NaOD in D_2O.

The limiting values of the ion conductances of OH^- and of OD^- in ordinary and in heavy water respectively have been computed.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, JOHNS HOPKINS UNIVERSITY]

Adsorption of Hydrogen and Nitrogen on Chromium Oxide Gel

BY P. H. EMMETT[1] AND MARTIN CINES[1a]

A number of years ago the late J. Howard[2] contributed one of the clearest indications that the activated adsorption of hydrogen on chromium-oxide gel was really a surface adsorption and not an activated diffusion of hydrogen into the particles of gel to form a solid solution. He found that the activated adsorption of 75 cc. of hydrogen on 37.5 g. of gel caused a decrease of about 50% in the physical adsorption of hydrogen at −78° and a 40% decrease in the physical adsorption of nitrogen at 0°. However, at the time his experiments were performed there was no good means available for judging the surface area and the size of the pores in the gel. His results could only be interpreted reasonably by assuming that much of the adsorbing surface was located in pores so small that they could be completely blocked by a layer of hydrogen held tightly by activated adsorption. Since very few examples have come to light of the inhibiting effect of activated adsorption on physical adsorption and, since a method is now available[3,4,5] for measuring the surface area and judging something as to the pore size,[6] it seemed worthwhile to repeat his results on a similar sample of chromium oxide gel.

Experimental Procedure

A sample of chromium oxide gel was prepared by the method used by Howard and originally described by Lazier and Vaughen.[7] To a liter of 0.04 *M* chromic nitrate was added slightly more than a liter of 0.12 *M* ammonium hydroxide. The excess ammonium hydroxide was required to help form flocs. The precipitate was washed by decantation ten times with the original volume of water. The gel was then filtered, and dried at 150°; 2.33 g. was taken as a sample.

The adsorption and surface area measurements were made in a standard adsorption apparatus that has already been described.[8] The dead space in the adsorption bulb was calibrated in the usual way with pure helium at the temperature of each run. Dried tank hydrogen and prepurified tank nitrogen were used as the adsorbates.

Results and Discussion

The nitrogen adsorption isotherm for the sample of gel as measured at −195° is shown in Fig. 1. The B.E.T.[4] plot indicates an area of 310 sq. meters per gram. The nitrogen monolayer on the 2.33-g. sample contained 165 cc. of nitrogen (S.T.P.). The isotherm is the normal S-shaped

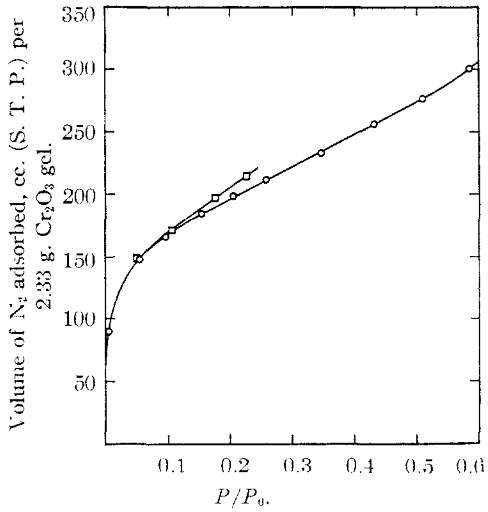

Fig. 1.—Influence of chemisorbed hydrogen on the physical adsorption of N_2 at −195° on chromic oxide gel: ○, N_2 adsorption before hydrogen chemisorption; □, N_2 adsorption at −195° after chemisorption of 8.3 cc. of hydrogen at 150°.

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[2] Howard, *Trans. Faraday Soc.*, **30**, 278 (1934).

[3] Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

[4] Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

[5] Emmett, *Ind. Eng. Chem.*, **37**, 639 (1945).

[6] Ries, Van Nordstrand, Johnson and Bauermeister, THIS JOURNAL, **67**, 1242 (1945).

[7] Lazier and Vaughen, *ibid.*, **54**, 3080 (1932).

[8] Emmett, "Am. Soc. Testing Materials, Symposium on New Methods for Particle Size Determination," 1941, p. 95.

variety characteristic of solids whose pores are much larger than molecular diameters.

Since we wished to determine the influence of chemisorbed hydrogen on the physical adsorption of both hydrogen and nitrogen, adsorption measurements were made for these two gases at various temperatures before introducing any chemisorbed hydrogen. The results are plotted in Fig. 2. The open circles represent, the adsorption for hydrogen at −195°, hydrogen at −78°, and nitrogen at 0°. The isotherms at −78° for hydrogen and 0° for nitrogen are approximately linear with pressure.

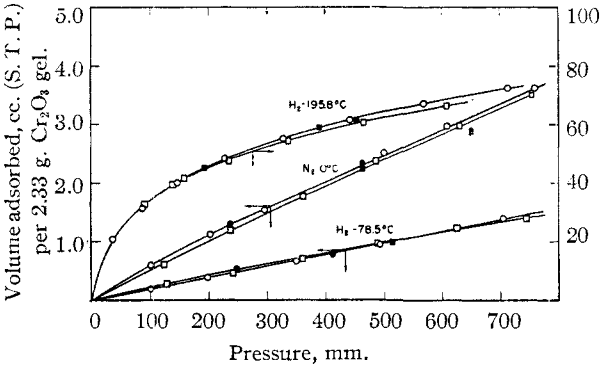

Fig. 2.—Influence of chemisorbed hydrogen on the physical adsorption of hydrogen at −195.8°; H_2 at −78.5°; and N_2 at 0°. Circles represent adsorption *before* putting 8.31 cc. of chemisorbed H_2 on the gel; squares show the adsorption after the chemisorption of 8.31 cc. of H_2. Solid circles and squares are desorption points.

To test the effect of chemisorbed hydrogen, 8.31 cc. was adsorbed at about 150°. This was the net adsorption after quickly degassing the sample at 150°, using the gas buret as a Töpler pump. This adsorption is even larger, per gram, than the one used by Howard. He chemisorbed 75 cc. on 37.5 g. of gel.

After the chemisorption of the hydrogen, physical adsorption runs for hydrogen were made at −195 and −78°; runs for nitrogen were made at −195 and 0°. The results after the hydrogen chemisorption are shown by squares in Figs. 1 and 2. It is apparent that the chemisorbed hydrogen caused no detectable decrease in the adsorption of either hydrogen or nitrogen at any of the temperatures or conditions employed.

The cause of a discrepancy of this kind is difficult to establish with certainty. In spite of the similarity of procedure there is some indication that his gel contained smaller pores and, therefore, might respond differently from ours, as regards the inhibitive effect of hydrogen. Perhaps his gel had smaller pores than our sample as a result of having been dried up to 400°, whereas ours was dried to only about 150°. Consistent with this explanation is the fact that his hydrogen isotherm at −78° and nitrogen isotherm at 0° were concave to the pressure axis whereas these isotherms on our samples are almost linear. This possible difference in pore structure seems to be the only reasonable explanation of the observed discrepancy; certainly there seems to be no question but that his experiments were carefully done and probably represent correct isotherms on his sample of chromium oxide gel.

Howard[2] used his findings to prove that activated adsorption of hydrogen on chromium oxide gel was a surface adsorption rather than a solution effect. As he pointed out other adsorption and catalytic observations also seem to establish the existence of activated adsorption as a surface phenomenon. For example, the activated adsorption of hydrogen[9] on iron catalysts strongly inhibits the activity of the catalysts for the interconversion of ortho–para hydrogen[10] at liquid nitrogen temperatures. This could hardly occur if the hydrogen held by activated adsorption were located elsewhere than on the surface of the catalyst. As a matter of fact, Howard's results, unless they can be shown to be in error, are still perfectly good evidence of pore blocking by hydrogen that is held by activated adsorption and hence of the existence of this hydrogen as a surface adsorption on the particular sample of chromium oxide that he employed. Our results merely indicate that for chromium oxide prepared and dried under the conditions used in the preparation of our sample, hydrogen chemisorption does not inhibit the physical adsorption of either hydrogen or nitrogen.

Summary

The chemisorption of 3.57 cc. of hydrogen per gram of chromium oxide gel has been found to have substantially no influence on the physical adsorption of hydrogen at −195 and −78°, and of nitrogen at 0°. The difference between these results and the marked inhibition of physical adsorption reported by Howard is believed due to differences in the pore sizes of the two gels.

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[9] Emmett and Harkness, This Journal, **57**, 1631 (1935).

[10] Emmett and Harkness, *ibid.*, **57**, 1624 (1935).