[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDY OF THE ADSORPTION OF WATER VAPOR AND CARBON DIOXIDE BY SAMPLES OF MANGANESE DIOXIDE AND HOPCALITE CATALYSTS

BY C. E. LANNING[1]

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Some time ago work in this Laboratory showed the great activity of manganese dioxide either alone or when mixed with other metallic oxides as an oxidizing catalyst.

These catalysts are capable of considerable variation as to composition but all possess a fineness of texture that renders them highly porous. Owing to their highly porous nature they tend to adsorb vapors readily and in the presence of gases having a considerable tension of water vapor, for instance, are likely to become "poisoned" by the condensation of liquid within the pores of the material. For this reason it was a matter of some interest to investigate the adsorption isotherms of these substances, especially with respect to water vapor and carbon dioxide.

Finely divided manganese dioxide has played a prominent role in the preparation of the most active catalysts of this type; also the conditions under which this oxide is prepared affect considerably its catalytic activity. Among the factors influencing the catalytic activity of the product is the alkalinity of the medium in which the oxide is prepared and consequently the amount adsorbed by the oxide. This effect of alkali might be to alter the degree of subdivision of the manganese dioxide or to alter the character of its surface. It was thought that the effect of alkali treatment on the structure of manganese dioxide could be determined by a careful study of the adsorption isotherms of the manganese dioxide after various treatments and in this way information gained that would be useful in preparing catalysts of this type. In addition it was hoped that such study would throw some light on the poisoning of the catalyst by water vapor, the possible poisoning by carbon dioxide, and the existence of definite hydrates of manganese dioxide which might have some influence on the activity of the catalyst.

Materials

The manganese dioxide was prepared according to the method of Frèmy,[2] which has been found to give uniformly a very finely divided product and to produce the most active catalyst. All samples were taken from this material. In each case the sample was screened and the granules between six and ten mesh selected for experimentation. These were kept in sealed bottles until used.

Sample 1.—The oxide was separated from adhering water as completely as possible

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[1] The above article forms part of the author's dissertation submitted in June, 1920, for the Ph.D. degree and the work was carried out at the suggestion of J. C. W. Frazer.

[2] Fremy, *Compt. rend.*, **82**, 1231 (1876).

on a Büchner funnel with a water pump. It was then placed in a press and subjected for forty-eight hours to a pressure of several tons per square inch. It was then removed and dried in an air-bath at 110° for three hours.

Sample 2.—The oxide was separated from liquid water on a Büchner funnel as above and dried for three hours in an air-bath at 140°.

Sample 3.—The oxide was dried on a Büchner funnel as above and for three hours in an air-bath at 140°. The material was then placed in a U-tube and for several days a current of a 1% mixture of carbon monoxide and nitrogen was passed over it at a temperature of 140°. Nitrogen was selected as a diluent to guard against overheating and prevent reoxidation.

Sample 4.—The oxide was dried as far as possible on a Büchner funnel. It was then suspended in a 0.1 *N* solution of sodium hydroxide, stirred thoroughly and allowed to stand for twenty-four hours. It was again dried as much as possible on a Büchner funnel and then for three hours in an air-bath at 140°.

Sample 5.—This sample was the catalyst, containing 63% MnO_2 and 37% Ag_2O.

Experimental

That these materials are very sensitive to changes in the moisture content of the air is shown by the following table giving results obtained by exposing two samples to the atmosphere alongside each other.

TABLE I

EXPERIMENTAL RESULTS

(1) a, 5.4762; b, 6.8397

Date	Sample a	Sample b	Pressure H_2O in air	% gain in wt. a	b
7/26/1919	6.0068	7.4990	15.25 mm.	9.69	9.64
27	6.0391	7.5401	17.45	10.28	10.24
29	5.8193	7.2696	8.05	6.266	6.285
8/3/1919	5.8642	7.3271	9.5	7.086	7.127
7	6.0841	7.6092	19.35	11.101	11.250

Part I: Adsorption of Water Vapors

The apparatus used for the study of the adsorption of water vapor consisted of a series of ten glass bulbs containing sulfuric acid of different but known concentrations, to establish definite vapor pressures in the system. The concentration of acid used varied from pure water in Bulb 1 to concentrated sulfuric acid in Bulb 10. These bulbs were all sealed to the apparatus and each could be shut off from the remainder of the system by a mercury trap. The sample to be investigated was weighed into a small glass bulb which was provided with a ground-glass stopper and a side tube with a stopcock, which was attached to the system by means of a ground-glass joint. The whole apparatus was contained in an air-bath, the temperature of which was kept constant within 0.10 of a degree. Before beginning the measurements permanent gases were removed from all parts of the system, including the sulfuric acid contained in the bulbs mentioned above, and the small bulb containing the sample. The removal of the air dissolved in the bulb containing pure water, and those containing dilute sulfuric acid, was much more difficult than the removal from the bulb containing strong sulfuric acid; in fact, the permanent gases were given off quite readily from strong sulfuric acid, and the ease with which the dissolved gases could be removed appeared to vary, rather regularly, with the concentration of the acid. The removal of the permanent gases from the whole system is of very great importance, as it has been found that a small concentration of these permanent gases greatly delays the establishment of equilibrium. The manipulation of all parts of the apparatus was accomplished without the necessity of opening the bath. The vapor pressures in the system were determined by means of a cathetometer. The temperature of the bath during this investigation was 35°. The experimental results are shown below in Fig. 1, where, for comparison, there is included a graph of the values obtained by Anderson[3] at 18° for silica gel.

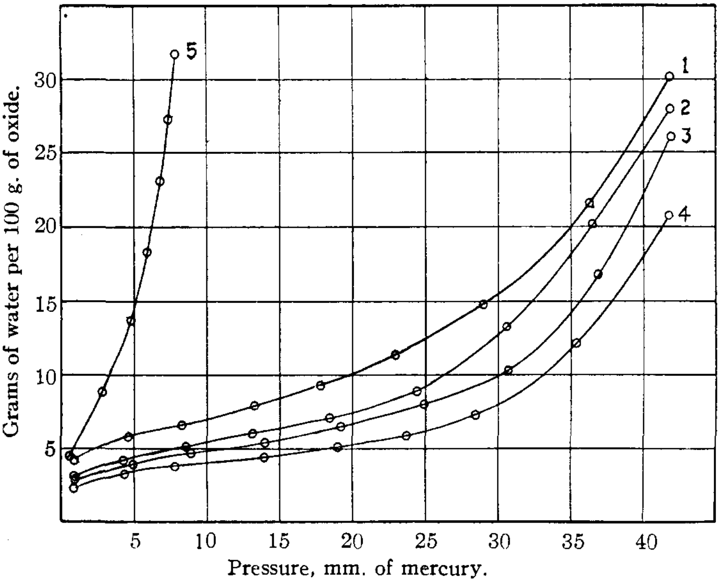

Fig. 1.—Adsorption of water vapor at 35°.

Part II. The Adsorption of Carbon Dioxide

The apparatus used for this part of the investigation was essentially that described by Patrick and McGavack.[4] The bulb containing the sample under investigation was kept at 0° by immersion in ice contained in a Dewar flask. The carbon dioxide used was obtained from a small cylinder of the gas, after allowing the permanent gases to escape as completely as possible. Here, again, permanent gases were removed completely from

[3] Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

[4] Patrick and McGavack, THIS JOURNAL, **42**, 946 (1920).

the whole system before the experiments were begun. The apparatus was carefully calibrated so that, from readings taken with the cathetometer, all of the data could be obtained for the accurate determination of the volume of carbon dioxide introduced into the system and the amount adsorbed at each stage by the sample. The results obtained are given in the form of curves in Fig. 2; again for comparison, the data on the adsorption of carbon dioxide by silica gel, as determined by Patrick,[5] were given. The only departure made in the regular routine procedure adopted was in the case of the sample which in its preparation had been exposed to a solution of caustic soda. In this case the sample was exposed for a considerable length of time to the action of carbon dioxide, which was subsequently pumped out of the apparatus before the experiment was begun.

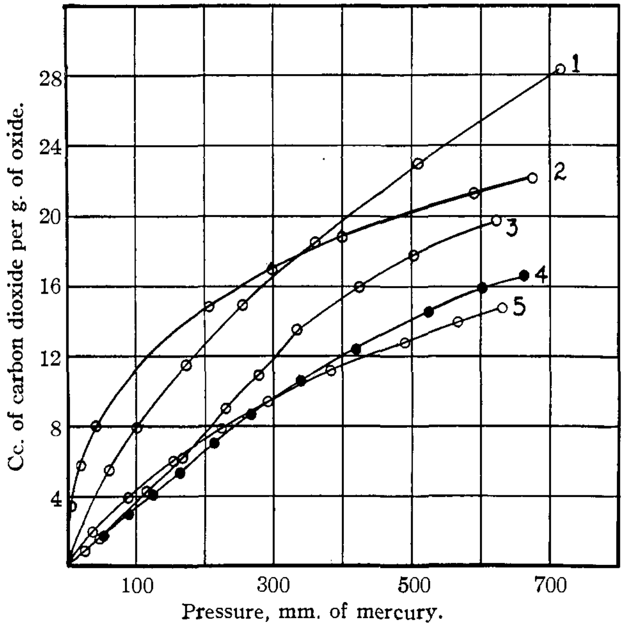

Fig. 2.—Adsorption of carbon dioxide at 0°.

Discussion

Since each point on the curves was duplicated, it is reasonably sure that they represent equilibrium conditions. This conclusion is made more definite because of the care taken in the complete removal of permanent gases from the system. Other work in this Laboratory has shown that in the presence of permanent gases it is very difficult to get true equilibrium in adsorption of vapors. These results show: (1) the highly porous, finely divided nature of all of these samples. Calculation of the approximate size

[5] Patrick, "Inaugural Dissertation," Göttingen, 1914.

of the pores from the experimental data given above is not regarded as justifiable, but does indicate that the internal surface of these oxides is very high. (2) The adsorption curve of the sample prepared in the presence of caustic soda does not differ materially from the other curves, and the effect of alkali in depressing the catalytic activity of these oxides cannot be due to a change in the physical structure of the oxide. Other work in this Laboratory[6] has shown that when finely divided manganese dioxide is prepared in the absence of alkali it is extremely active catalytically. The effect of the alkali adsorption must, therefore, be that of a so-called "catalytic poison." (3) There is no evidence from any of these curves for the existence of definite hydrates.

Summary

The author has investigated the adsorption of water vapor and carbon dioxide on samples of finely divided manganese dioxide and mixtures of this oxide with other metallic oxides. The results are given in the form of curves and the shape of these curves shows that in neither case is there evidence of the formation of definite chemical compounds, but brings out clearly the very fine porosity of these substances.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

CYANOGEN IODIDE AS AN IMPURITY IN IODINE. ITS DETECTION AND ELIMINATION

BY SAMUEL MORRIS, E. B. CALLAGHAN, AND LUCILE DUNLAP

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Cyanogen iodide is commonly considered one of the chief impurities in commercial iodine. According to Dammer[1] iodine has been known to contain as high as 28.75% of this impurity. Baxter,[2] in his work on the atomic weight of iodine, took great care to eliminate cyanogen iodide. In the method which he used, iodine was suspended in water and treated with hydrogen sulfide, which formed hydriodic acid and, in case cyanogen iodide was present, hydrocyanic acid also. The separation of these two acids, as employed by Baxter, involved long-continued boiling and was based upon the separation of hydrochloric and hydrocyanic acids by the method of Richards and Singer.[3]

In the present paper, study was made first of the separation of known mixtures of hydriodic and hydrocyanic acids. This suggested a procedure for the detection of small quantities of –CN in iodine, which was worked out

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[6] Whitesell, THIS JOURNAL, 45, 2841 (1923).

[1] Dammer, "Handbuch der Anorg. Chem.," Vol. I, p. 542.

[2] Baxter, THIS JOURNAL, 26, 1579 (1904); 27, 876 (1905).

[3] Singer, *Am. Chem. J.*, 27, 205 (1902).