

The figure for zinc oxide  $\Delta H_{298} = -83,270 \pm 50$  (15° calories) is proposed as most acceptable on the basis of experimental work now available. The probable uncertainty of about 50 calories is nearly the same as may be inherent in the heats of formation of water as used. The experimental results confirm estimates by thermodynamic methods.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## THE ADSORPTION OF WATER AND BENZENE VAPORS BY MANGANESE DIOXIDE<sup>1</sup>

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Manganese dioxide is an active catalyst for the oxidation of carbon monoxide. Bray and his students<sup>2</sup> have made a very complete investigation of the properties of copper oxide-manganese dioxide catalysts. Bray and Draper<sup>3</sup> have determined water isotherms for these oxide mixtures at 25° and showed how these vapor isotherms could be used in determining the structure of the oxides. Whitesell and Frazer<sup>4</sup> have developed a method for preparing manganese dioxide, yielding a product which is a more active catalyst than the mixtures with other oxides. The present investigation deals with the adsorption of water and benzene by manganese dioxide prepared according to this method. The effects on the adsorption isotherms of temperature, temperature of outgassing, and the presence of permanent gases have been investigated and the results have been used to draw some conclusions with regard to the structure of the oxide and the mechanism of the adsorption process.

### Materials

The manganese dioxide used in the adsorption isotherms was prepared by sifting finely powdered C. P. potassium permanganate into concentrated nitric acid, according to the method of Whitesell and Frazer.<sup>4</sup> The suspension was stirred by a motor at a temperature of 25–30°. After complete reaction, the oxide was allowed to settle, then filtered and washed until the filtrate showed no test for nitrates. The product was dried for seventy-two hours at 110–115°. The product was then further washed by decantation and on the filter for a week. Different lots of this material were heated

<sup>1</sup> An abstract of a dissertation presented by J. K. Dixon to the Graduate School, Yale University, 1929, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Almquist and Bray, *THIS JOURNAL*, **45**, 2305 (1923); Hoskins and Bray, *ibid.*, **48**, 1454 (1926); Bray and Doss, *ibid.*, **48**, 2060 (1926).

<sup>3</sup> Bray and Draper, *Proc. Nat. Acad. Sci.*, **12**, 295 (1926); Draper, *THIS JOURNAL*, **50**, 2637 (1928).

<sup>4</sup> Whitesell and Frazer, *ibid.*, **45**, 2841 (1923).

at the temperatures desired, and were then analyzed. The temperatures and composition of the oxide after heating are given in Table I.<sup>5</sup> Manganese was determined as the pyrophosphate, available oxygen by the oxalate method, water by the Penfield method, and impurities by difference.

TABLE I  
TEMPERATURE OF HEATING AND COMPOSITION OF PRODUCT

Temperature of heating, °C.....	190	390	475
Ratio, O:Mn.....	1.93	1.85	1.51 <sup>a</sup>
Percentage of H <sub>2</sub> O.....	2.81	1.02	..
Percentage of impurities (by difference).....	0.32	1.64	..

<sup>a</sup> Oxide analyzed after use in a water isotherm.

The benzene used had been washed five times with mercury, four times with sulfuric acid, and then recrystallized twice. It was dried over sodium and distilled from this metal directly into the adsorption apparatus. The boiling point of the benzene was 80.04° at 760 mm.<sup>6</sup>

### Apparatus and Experimental Procedure

The adsorption isotherms were determined in an apparatus in which the amount of vapor adsorbed was determined by direct weighing. It is similar in principle to the apparatus described by Zsigmondy, Bachmann and Stevenson.<sup>7</sup> A diagrammatic sketch is shown in Fig. 1. The apparatus was of pyrex glass and was evacuated by means of a mercury pump which was backed by an oil pump. Pressures above 2 mm. were determined with an accuracy of  $\pm 0.05$  mm. by measuring the difference in height of the mercury column at N, by means of a cathetometer. Pressures from 0.001 mm. to 2 mm. were determined by means of a modified McLeod gage, L. It consisted of a bulb, D, of known volume, to which was attached the glass tubing, EFGHI. The section of tubing, EF, was of 12 mm. bore, FG was of 6 mm., and GHI was large capillary tubing. The volumes of the tubing and bulb were determined by calibration with mercury and water, respectively. The calibration figures are given in Table II.

TABLE II  
CALIBRATION DATA

	Volume, cc. per cm.	Length, cm.
GH	0.041	12.5
FG	.131	40.7
EF	.585	24.0

Volume of D (from J to E) = 186.4 cc.

The pressure of the vapor after compression was given by the difference in heights of the mercury columns at H and I. Since the volume of vapor before and after com-

<sup>5</sup> The second long washing noted above was subsequently found to be unnecessary. Two adsorption isotherms carried out with material which had only been subjected to the first washing showed nearly identical but slightly greater adsorption than the more thoroughly washed material.

<sup>6</sup> We are indebted to Dr. R. P. Smith of this Laboratory for this very pure product and for the boiling point determination.

<sup>7</sup> Zsigmondy, Bachmann and Stevenson, *Z. anorg. Chem.*, **75**, 189 (1912); Anderson *Z. physik. Chem.*, **88**, 191 (1914).

pression and the final pressure were known, the pressure in the apparatus could be easily calculated. The pressures calculated checked the values found at N when they were of the order of 1–2 mm. and were accurate to 2%. Coolidge<sup>8</sup> has pointed out that such a gage may give erroneous results below 0.01 mm. Our experimental results below this pressure, however, show no peculiar or irregular behavior and indicate that the pressures are correct.

The vapor used in the adsorption isotherms was distilled into Q through Q' in a vacuum produced by opening stopcock O. Distillation between the two bulbs a number of times, with intermittent pumping, served to remove any permanent gases dissolved.

The bulb, U, which contained the manganese dioxide, had a volume of 14.4 cc. X is a ground-glass stopper which was sealed with wax; T, a stopcock; and S, a ground joint. By unseating the bulb at S, after closing T, it was possible to determine the weight of the adsorption bulb with its contents. Ramsay grease was used at S and removed with ether before each weighing of U. Any weighing could be checked within

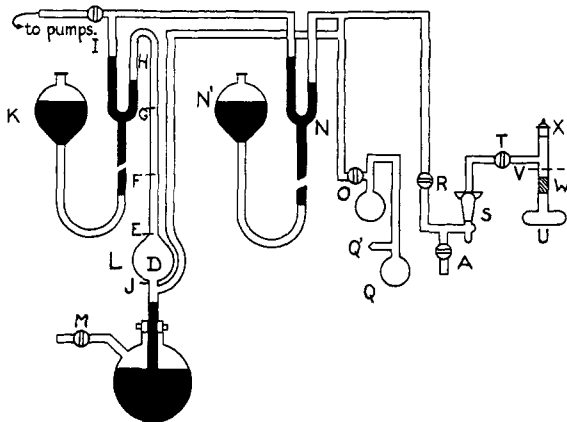


Fig. 1.

0.2 mg. after greasing the joint S again and recleaning. A small plug of ignited asbestos at W, weighing less than 0.2 g., prevented the adsorbent from flying out of the bulb when it was heated and outgassed. A preliminary experiment had shown that the vapor adsorbed by the asbestos was negligible.

The procedure in determining an isotherm was as follows. The weight of the evacuated adsorption bulb was found and from 3 to 4 g. of manganese dioxide introduced. The asbestos was introduced, the stopper put in place and sealed with wax, and the weight of wax and asbestos determined. By proper manipulation of stopcocks T and R and the leveling bulb, N', the adsorbent was pumped free of gases. A small platinum-wound furnace was drawn up about U and the bulb containing adsorbent was heated at the desired temperature while being subjected to the full vacuum produced by the pumps. The temperature was indicated by a calibrated thermometer clamped against the bulb, U, and could be kept constant within  $\pm 3^\circ$ . After outgassing in this manner, U was cooled and weighed. The actual weight of outgassed oxide could then be calculated.

The bulb, U, was now resealed at S and immersed in the thermostat, the tubing from R to T evacuated and a suitable amount of vapor admitted to the system through

<sup>8</sup> Coolidge, *THIS JOURNAL*, **46**, 596 (1924).

O. The stopcock, T, was then opened. The oxide adsorbed the vapor until equilibrium was reached, which was shown by a constancy of pressure. The time to reach equilibrium was four hours or longer, depending largely on the temperature. The weight of vapor taken up was found by removing and weighing the bulb, U. Each successive point in an adsorption isotherm was determined in a similar way, and it is apparent that either adsorption or desorption curves could be found. The weight of vapor adsorbed was corrected for the amount of vapor as such in the bulb.

Adsorption isotherms at 25 and 40° were obtained by immersing U in a well-stirred water thermostat up to the mark V. Isotherms at 0 and -17.46° were found by immersing the bulb in ice and water, and in the eutectic mixture of ice and sodium nitrate.<sup>9</sup>

Attempts were made to determine corresponding isotherms for carbon tetrachloride and certain alcohols, but they were unsuccessful, due to oxidation by the manganese dioxide.

### The Adsorption Isotherms for Water and Benzene

The data for a typical adsorption and desorption isotherm are given in Table III. The first column,  $p$ , gives the observed vapor pressure in millimeters of mercury and the second column,  $p/p_0$ , is the ratio of the observed vapor pressures to that of pure water at the temperature of the experiment (25°). The third column,  $q$ , gives the weight of water adsorbed by one gram of the outgassed oxide.

TABLE III  
ADSORPTION AND DESORPTION OF WATER BY MANGANESE DIOXIDE WHICH HAD BEEN  
OUTGASSED AT 190° (SEE TABLE I).  $t = 25^\circ$

$P$	$P/P_0$	$q$	$P$	$P/P_0$	$q$	$P$	$P/P_0$	$q$
0.0276	0.00116	0.0207	17.30	0.728	0.2166	16.20	0.682	0.2297
.137	.00577	.0295	17.60	.741	.2204	14.95	.630	.1885
.308	.0130	.0332	17.65	.743	.2276	14.80	.623	.1726
.903	.0380	.0401	18.50	.779	.2539	14.35	.604	.1538
3.65	.154	.0561	19.15	.806	.2674	13.30	.560	.1302
7.60	.320	.0707	20.70	.871	.2739	10.40	.437	.1027
10.45	.440	.0901	21.60	.909	.2766	6.70	.282	.0851
15.35	.646	.1432	18.70	.787	.2700	3.45	.145	.0737
16.00	.674	.1546	17.10	.720	.2592	2.10	.0885	.0668
16.75	.705	.1799	16.50	.695	.2398	1.50	.0633	.0626

The results are plotted in Fig. 2.<sup>10</sup> The broken lines between the two curves are taken from a subsequent experiment and illustrate the way transitions occur from desorption to adsorption curves, or the reverse. Hysteresis is present and, as so often in other cases, seems to be due to some property of the adsorbent. Lambert and Clark<sup>11</sup> observed hysteresis

<sup>9</sup> "International Critical Tables," Vol. IV, p. 259.

<sup>10</sup> The time allowed for the system to reach equilibrium extended overnight in some cases, but these points show no regular deviation from points determined in the usual way.

<sup>11</sup> Lambert and Clark, *Proc. Roy. Soc. (London)*, **117A**, 183 (1927); *ibid.*, **122A**, 497 (1929).

in the adsorption of benzene by ferric oxide; with the same apparatus and experimental procedure, they found none in the adsorption of benzene by silica gel. Since each isotherm exhibited hysteresis phenomena exactly similar to that shown in Fig. 2, only the adsorption curves will be considered in the subsequent curves and discussion.

Figure 3 shows the adsorption isotherms of water on the oxide (outgassed at  $190^{\circ}$ ) at the temperatures  $-17.5$ ,  $0$ ,  $25$  and  $40^{\circ}$ . Here  $\log q$  is plotted against  $\log p$ ,  $q$  and  $p$  representing, as before, the weight of water adsorbed per gram of oxide, and the corresponding pressure. The iso-

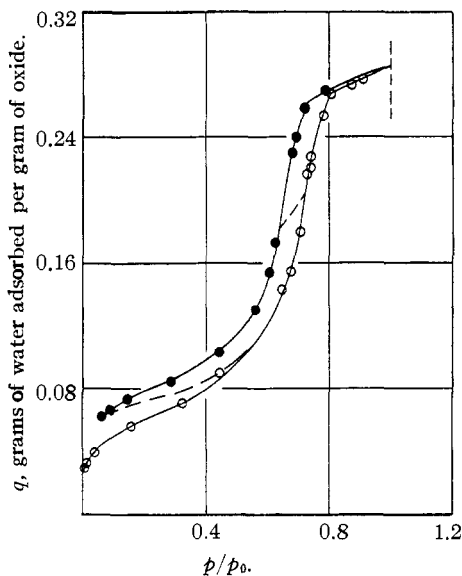


Fig. 2.—Adsorption isotherm for water on manganese dioxide at  $25^{\circ}$ :  $\circ$ , adsorption;  $\bullet$ , desorption.

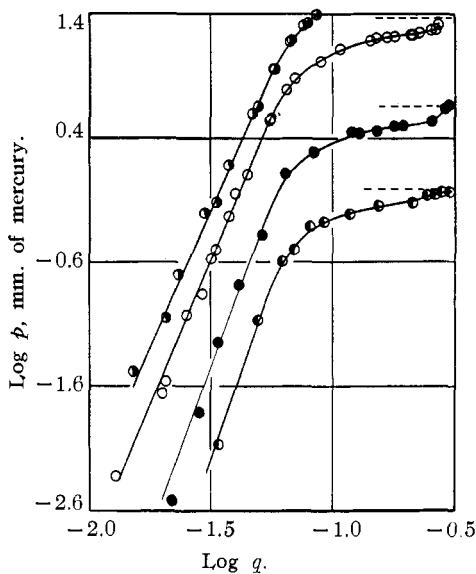


Fig. 3.—Adsorption isotherms for water on manganese dioxide:  $\circ$ ,  $40^{\circ}$ ;  $\circ$ ,  $25^{\circ}$ ;  $\bullet$ ,  $0^{\circ}$ ;  $\bullet$ ,  $-17.5^{\circ}$ .

therms at  $25$  and  $40^{\circ}$  are each plots of two separate series of determinations and show that, with a fixed method of treatment, the oxide gives reproducible adsorption curves. The two series at  $25^{\circ}$  were determined three months apart, showing that the oxide did not change during this time. Also, the water used in the later series had been standing in the apparatus for two months in the absence of air with occasional intermittent pumping, so that the presence of traces of gases from this source is excluded. The adsorption isotherms of benzene on the oxide (outgassed at  $190^{\circ}$ ) were determined at  $0$  and  $25^{\circ}$  and the results are shown (together with two other isotherms mentioned later) in Fig. 4.

The isotherms for water and benzene show that these vapors are adsorbed at lower pressures in the same way that permanent gases are adsorbed by

charcoal, since the  $\log p$ - $\log q$  curves are nearly straight. It is reasonable to assume that pure surface adsorption is taking place over this range of pressures. At a value of  $p/p_0$  of about 0.5, the isotherms break rather sharply and the amount of vapor adsorbed increases rapidly with a small increase in pressure. If this great increase in the rate of adsorption is due to condensation in the capillary spaces of the oxide,<sup>12</sup> the radii of the capillary spaces can be calculated by means of Thomson's equation.<sup>13</sup> Such calculations for water and benzene at different temperatures give values which are in good agreement, the capillaries having radii extending from 10 to 40 Å. Shereshefsky<sup>14</sup> has shown that for very small capillaries, however, the surface tension of the condensing liquid is not normal, and Polanyi and Goldmann<sup>15</sup> have shown that the density of an adsorbed liquid is greater than that of the free liquid. For these reasons, it is doubtful if calculations by the Thomson equation have more than qualitative significance.

Polanyi has developed<sup>15,16</sup> an expression for the so-called adsorption potential which, so far as it is applicable, can be used to calculate the adsorption isotherms for a given adsorbent and vapor at any temperature when one isotherm is known.

$Aq$ , the adsorption potential, is given by the equation:  $Aq = RT \ln (p_0/p)$ , in which  $R$  is the gas constant,  $T$ , the absolute temperature and  $p$  and  $p_0$  have their usual significance. Plotting  $Aq$  against  $q$ , the curves should coincide at all temperatures, if correction is made for the change with temperature of the density of the adsorbed vapor. When their results were uncorrected for density changes, Polanyi and Goldmann<sup>15</sup> found experimentally that a lower temperature curve fell above a higher temperature curve in the cases of chloroform, carbon bisulfide, ether and pentane ad-

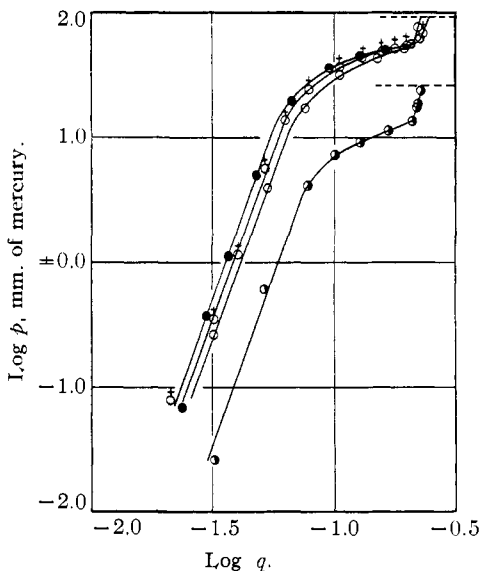


Fig. 4.—Curves showing the adsorption isotherms of benzene on  $MnO_2$ :  $\bullet$ ,  $0^\circ$ ;  $\circ$ ,  $25^\circ$  (oxide outgassed at  $190^\circ$  in both isotherms);  $\delta$ ,  $25^\circ$ , oxide outgassed at  $290^\circ$ ;  $\bullet$ ,  $25^\circ$ , same as last with oxide outgassed two hours more at  $190^\circ$ .

<sup>12</sup> Hückel, "Adsorption und Kapillarkondensation," Part III, Leipzig, 1928.

<sup>13</sup> Thomson, *Phil. Mag.*, [4] **42**, 448 (1871).

<sup>14</sup> Shereshefsky, *THIS JOURNAL*, **50**, 2966, 2980 (1928).

<sup>15</sup> Polanyi and Goldmann, *Z. physik. Chem.*, **132**, 321 (1928).

<sup>16</sup> See also Lowry and Olmstead, *J. Phys. Chem.*, **31**, 1601 (1927).

sorbed by charcoal. In Fig. 5 our data for water and benzene, uncorrected for density changes, have been plotted in the same way. The coincidence of the curves, on the whole, is surprisingly close. The curves for water are almost identical except at  $-17.5^\circ$  for high values of  $p/p_0$ , where the difficulties of accurate determination are great. Polanyi's theory postulates surface adsorption and, subsequently, liquefaction of the adsorbed vapor, which is in accord with the theory of capillary condensation. The two theories differ in that they propose different causes of liquefaction. The theory of Polanyi has proved to be the more useful.

### The Effect of the Temperature of Outgassing

Almquist and Bray<sup>17</sup> have shown that the catalytic activity of CuO-MnO<sub>2</sub> mixtures decreased as the temperature of dehydration was increased above 200°. Drucker and Hüttner<sup>18</sup> have shown that when manganese dioxide is heated, it loses oxygen somewhat irreversibly, forming a lower oxide on the outside of the particles. We have investigated the effects of the temperature of outgassing on the adsorption isotherms in order to show the surface and other structural changes taking place on heating.

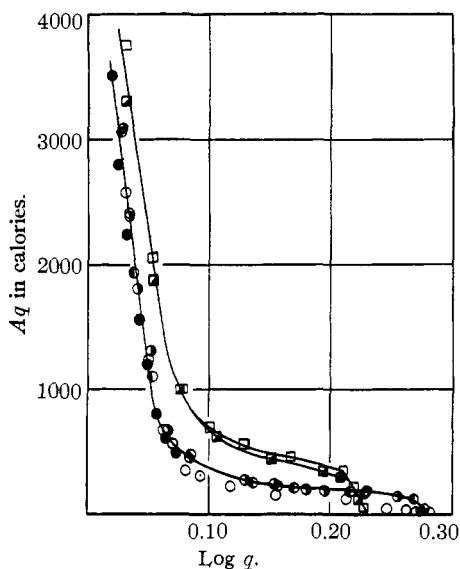


Fig. 5.—Adsorption potential curves for water and benzene on manganese dioxide. Water: ○,  $-17.5^\circ$ ; ●,  $0^\circ$ ; ○,  $25^\circ$ ; ●,  $40^\circ$ . Benzene: □,  $0^\circ$ ; ■,  $25^\circ$ .

Water isotherms at  $0^\circ$  were determined (a) on a sample previously used for a  $0^\circ$  isotherm and which was then heated at  $390^\circ$  for three hours, and (b) on a sample heated at  $475^\circ$  for three hours. These two isotherms, together with one on material heated normally at  $190^\circ$ , are plotted in Fig. 6. The diagrams show that preliminary heating has a marked effect on the adsorption curves only when the temperature is so high ( $475^\circ$ ) that

<sup>17</sup> Almquist and Bray, *THIS JOURNAL*, **45**, 2305 (1923).

<sup>18</sup> Drucker and Hüttner, *Z. physik. Chem.*, **131**, 237 (1928).

the composition of the oxide is materially changed, as shown by Table I. On this high-temperature oxide, both surface adsorption and that attributed to capillary condensation are markedly decreased, due to sintering or to the formation of an inactive lower oxide, or both. When capillary condensation begins on this oxide the capillaries have radii of 54 Å. (using the Thomson equation), which is three times the value found for the oxide outgassed at 190°. The accompanying decrease in surface area will not account for more than one-tenth of the decrease in surface adsorption at low pressures. Hence, the state of the surface as well as its area is important in the adsorption process. The surface adsorption of water vapor is a measure of the ability of the oxide to take up a gas by primary adsorption, and Benton<sup>19</sup> has pointed out that this adsorption is a measure of catalytic activity as far as the oxidation of carbon monoxide is concerned. It is probable that the parts of the vapor isotherms due to capillary condensation yield information only with regard to surface area and uniformity of the capillary spaces and are otherwise useless in predicting catalytic phenomena.

The oxide outgassed at 475° corresponds closely to Mn<sub>2</sub>O<sub>3</sub>. Its water isotherm showed very little hysteresis, and for this reason it is probable that the manganese dioxide is the cause of any difference between the adsorption and

desorption curves of an isotherm, rather than traces of any gas. If, for instance, adsorbed oxygen coats the oxide particles and causes hysteresis at lower outgassing temperatures, there appears to be no reason why it should not do so when the outgassing temperature is increased, with correspondingly increased oxygen pressure.

### The Effect of the Presence of Permanent Gases

If a permanent gas is adsorbed on the surface of the manganese dioxide, it should cover the most active adsorbing patches and reduce the area available for the surface adsorption of a vapor. Capillary condensation (or condensation caused by forces acting between adsorbent and vapor)

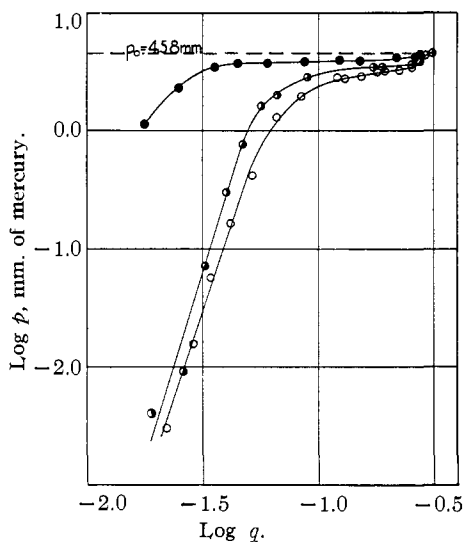


Fig. 6.—Curves showing the effect of the temperature of outgassing on the water isotherms for MnO<sub>2</sub> at 0°. Temperature of outgassing: ○, 190°; ◐, 390°; ●, 475°.

<sup>19</sup> Benton, THIS JOURNAL, 45, 887, 900 (1923).



should be little affected by the presence of permanent gases. This was found to be the case experimentally. The effects of adsorbed carbon monoxide and carbon dioxide were entirely similar to each other, so the results for the former will be given as typical of both.

**Experiment 1.**—Carbon monoxide, which had been dried carefully by passing through sulfuric acid and phosphorus pentoxide, was admitted to a sample of manganese dioxide which had been outgassed as usual at  $190^\circ$  for three hours. The equilibrium pressure of the gas after adsorption was 29.6 mm. The gas was then removed by pumping for one hour and the water isotherm at  $25^\circ$  determined.

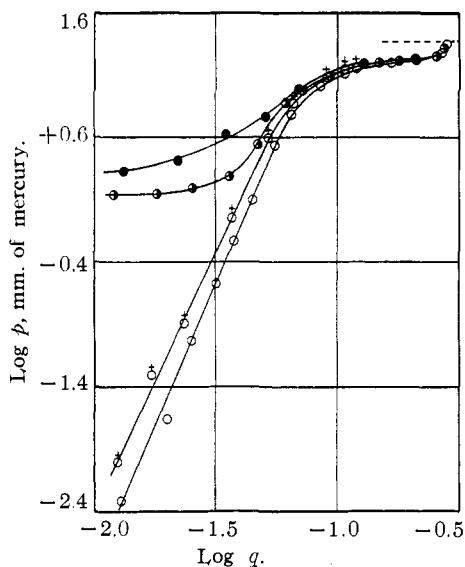


Fig. 7.—Curves showing the effect of the presence of carbon monoxide on the water isotherms for  $\text{MnO}_2$  at  $25^\circ$ : O, carbon monoxide absent; O with a dot, carbon monoxide present; ●, carbon monoxide present (greater amount); O with a cross, same, after outgassing at  $190^\circ$ .

These experiments with the three gases show rather definitely that the vapor isotherms run on the outgassed oxide have been measured on an oxide surface and not on a surface covered with oxygen. Carbon monoxide and carbon dioxide cover the active adsorption patches, reducing the surface adsorption of water, while oxygen has no effect. Condensation of water on the adsorbent (which occurs at the higher pressures) is not

**Experiment 2.**—Similar to Experiment 1; equilibrium pressure of carbon monoxide 88.5 mm. The gas was removed by pumping for one and one-half hours; pressure after standing for twelve hours, 0.215 mm. The gas was again pumped off for one hour, and the water isotherm determined as before. The oxide was then outgassed at  $190^\circ$  and the water isotherm redetermined. The results of the three isotherms are plotted in Fig. 7. It is evident that surface adsorption has been markedly reduced, the effect being greater at lower pressures. There is no effect on that portion of the water isotherm attributed to capillary condensation. Very possibly the water displaced some of the permanent gas from the surface, which would mean that the pressure of the water vapor was less than that measured, but this would merely decrease the difference between a treated and untreated oxide. This error would be negligible at pressures where condensation begins. The experiments with oxygen were carried out similarly.

**Experiment 3.**—(Run in duplicate.) After outgassing the oxide, dry

oxygen was admitted at a pressure of 135 mm. There was no evidence of adsorption. After evacuating and allowing the apparatus to stand for twelve hours, the pressure was less than  $10^{-4}$  mm. The water isotherm was then determined as before at  $25^\circ$ . This was identical, within the errors of the experiment, with an isotherm run on the outgassed oxide, which had not been treated with oxygen, and the hysteresis had not been changed.

These experiments with the three gases show rather definitely that the vapor isotherms run on the outgassed oxide have been measured on an oxide surface and not on a surface covered with oxygen. Carbon monoxide and carbon dioxide cover the active adsorption patches, reducing the surface adsorption of water, while oxygen has no effect. Condensation of water on the adsorbent (which occurs at the higher pressures) is not

measurably affected by the permanent gases. Heating removes the permanent gas which is adsorbed, cleaning up the surface of the oxide, and restores the surface adsorption of water vapor to its normal value.

### Summary

The adsorption isotherms of water on manganese dioxide have been determined at  $-17.5$ ,  $0$ ,  $25$  and  $40^\circ$ , and corresponding isotherms for benzene at  $0$  and  $25^\circ$ . The isotherms consist of two parts due to surface adsorption and condensation of the vapor on the surface of the oxide. Polanyi's theory of adsorption is in agreement with the data.

When the temperature of outgassing is raised, the surface adsorption for water is greatly reduced, due to the destruction of active adsorption patches. The treatment of the oxide with a permanent gas which can be adsorbed reduces the surface adsorption of water vapor and leaves the part of the isotherm due to condensation unaltered. The use of vapor isotherms in predicting the catalytic behavior of an oxide has been discussed.

The isotherms exhibit hysteresis and the present experiments indicate that this phenomenon is not due to false equilibrium or the presence of permanent gases on the surface of the oxide.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY COLLEGE OF SCIENCE]

## MEASUREMENTS OF THE ELECTROMOTIVE FORCE OF THE CALOMEL ELECTRODE AGAINST THE HYDROGEN ELECTRODE AT LOW CONCENTRATIONS OF HYDROCHLORIC ACID

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### Introduction

It is well known that the calomel electrode is not reliable at concentrations of hydrochloric acid below  $0.03 N$ .<sup>1</sup> There is a difference of opinion as to the causes responsible for the unreliability of calomel electrodes.<sup>2</sup> Our observations generally corroborate previous authors and deal with the questions (a) how far the observed potential can be taken as a measure of the actual concentration of the hydrochloric acid in the cell, and (b) the nature of the chemical reactions responsible for the observed change in concentration.

### Experimental

The chemicals used were Merck's "Reagent" or Kahlbaum's "pro analyse" quality purified as usual. The hydrogen was obtained from electrolysis of a strong solution of

<sup>1</sup> Ellis, *THIS JOURNAL*, **38**, 737 (1916); Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

<sup>2</sup> See Clark, "Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, 3rd ed., **1928**, p. 309.