Summary

1. Measurements at 25° of the cells

$$H_2 \mid KOH(m_1), KCl(m_2) \mid K_xHg \mid KOH(m_1) \mid H_2$$

in which $(m_1 + m_2)$ was kept at a constant molality of 3.5 have been made.

2. Similar measurements of the cells

$$H_2 \mid NaOH(m_1), NaCl(m_2) \mid Na_xHg \mid NaOH(m_1) \mid H_2$$

at total molalities of 3 and 5 have been presented.

3. From these data the activity coefficients of the hydroxides in the chloride solutions have been computed.

4. The linear relationship given by Equation 1 does not hold for the activity coefficients of the hydroxides in these mixtures. The differences between the observed and calculated activity coefficients were not very large. The maximum difference which occurred with the 5 *M* sodium hydroxide–chloride mixtures was 3.9%.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC OXIDATION OF CARBON MONOXIDE.

IV. THE PORE VOLUME OF THE CATALYSTS MANGANESE DIOXIDE, COPPER OXIDE AND MIXTURES OF THESE OXIDES

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RECEIVED JUNE 22, 1928 PUBLISHED OCTOBER 6, 1928

In this paper are presented the results of experiments, completed in 1922, on the pore volume and related physical properties of the catalysts investigated and reported on in the first papers of this series.[1] Results of tests upon the catalytic efficiency of related series of catalysts, in which the composition varied between MnO_x (where x is less than 2) and CuO, showed that all the mixtures were more catalytically active than either of the pure components, whether the mixing was effected by thorough kneading of the moist hydrated oxides with subsequent drying,[1a] or by stirring together finely ground portions of the previously dried or ignited components.[1c] These results point to the conclusion that the component oxides retain their characteristic properties in the mixtures and that the "mixture effect" is due to a speeding up of the electronic rearrangement postulated in the mechanism for the catalytic reaction.[2]

As in the previous papers, the members of the three series reported on here (Almquist's Series 1, 2 and 3) will be referred to by the numbers from 1 to 6, in the order of decreasing manganese dioxide content. The compo-

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[1] (a) Almquist and Bray, THIS JOURNAL, **45**, 2305 (1923); (b) Hoskins and Bray, *ibid.*, **48**, 1454 (1926); (c) Bray and Doss, *ibid.*, **48**, 2060 (1926).

[2] Ref. 1 b, pp. 1470–1473.

sitions of these catalysts with respect to CuO, MnO_x, H_2O, CO_2 and impurities are given in the first paper.

Definitions of Terms Used.—In the following, "true density" shall indicate that value of the density obtained by immersing the evacuated granules beneath gas-free water and determining the loss of weight sustained. This value will represent the actual density of the solid only if there is no expansion or contraction of the water in the pores of the granule and if all the pores are completely filled. Neither of these conditions is actually fulfilled in all probability.

"Granule density" will indicate the mass in grams of a granule having the volume of one cubic centimeter. This volume will consist of the volume of the solid plus the intra-granular volume (pore volume).

"Apparent granule density" or "apparent density" will indicate the value obtained by filling a vessel with granules, settling them by gentle tapping, and dividing the mass of the granules by the volume of the vessel.

The entire intra-granular free space will be called the "pore volume," which consists of "micro-capillaries," "macro-capillaries" and "cavities."

Part I of the paper will give the results of the determination of the total pore volume and the related properties of the granules; Part II will give the results from which a knowledge of the distribution of the pore volume between micro-capillaries, macro-capillaries and cavities can be obtained.

Part I

Experimental.—The true densities of the granules of Series 1 and 2, and the three samples prepared at Washington, were determined by the method of Hulett.[3]

From 4 to 8 g. of the granules was placed in a Pyrex tube constructed as shown in Fig. 1, which was then sealed off at A. Tube B was then sealed to a vacuum line and the granules were evacuated at about 200° for from three to seven hours. Eight tubes were sealed to a ring close enough together to be immersed in the same heating bath, thus insuring that all of the granules of a given series received uniform treatment. When the pressure had fallen to about 0.003 mm., the tubes were sealed off at C.

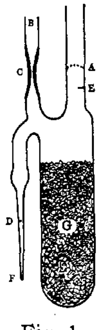

Fig. 1.

After cooling, each tube was cleaned, scratches were made at D and E and its weight reduced to *vacuo* was determined. Tube F was then inserted in tube H of the Pyrex "wash-bottle," Fig. 2, which contained distilled water, the two tubes being joined together by tight fitting rubber tubing. The water in the wash-bottle was then freed from dissolved gases by boiling under reduced pressure, and the gas-free water introduced into the granule tube by breaking the capillary at D.

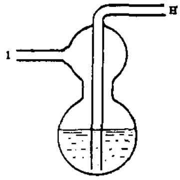

Fig. 2.

The density and pore volume of the granules was then determined as described by Cude and Hulett.[3]

Since it appeared from the results of Series 1 and 2 that a high degree of precision

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[3] Cude and Hulett, This Journal, **42**, 391 (1920).

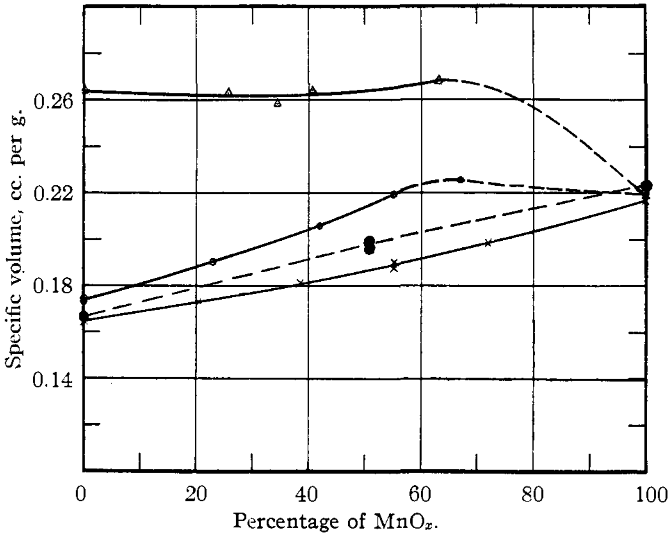
in the true density was not essential, a somewhat simpler method was used in this determination for Series 3.

Duplicate determinations made upon different specimens of the same sample gave a satisfactory check, as shown below.

CHECK RESULTS ON TWO SPECIMENS OF SAMPLE 5, SERIES 1 (WASHED)

True density, g. per cc.	4.436	4.433
Specific volume, cc. per g.	0.2255	0.2256
Pore volume, cc. per g. of solid	0.49	0.50
Pore volume, cc. per cc. of solid	2.16	2.21
Granule density, g. per cc.	1.41	1.38

All the granules (Series 1 had to be washed free of soluble salts[4]) showed an initial "drift" in the density such as Hulett[3] and Harkins[5] found in experiments with charcoal, but of much smaller magnitude and of much shorter duration. None of these oxide granules required more than a



○ Series 1 (washed); × Series 2; △ Series 3; ● Washington samples.

Fig. 3.

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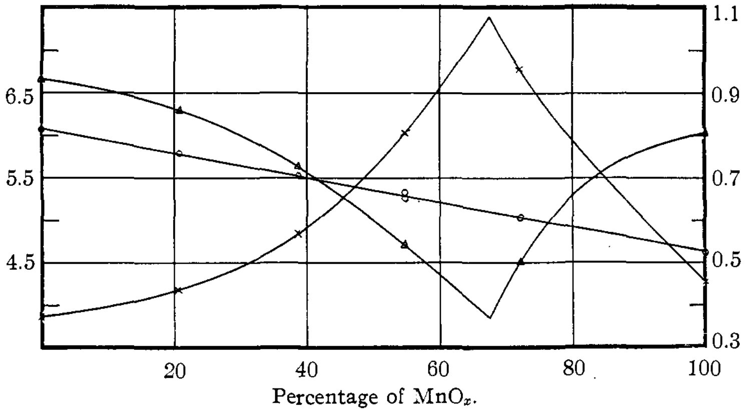
[4] Granules of Series 1 gave an unexpected result in showing a large drift almost exactly as described by Hulett and Harkins *but in the opposite direction.* Thus a 7g. specimen of Sample 6 changed from a density of 5.68 to 4.69 between Sept. 23 and Jan. 26, a change of 21%. From its mode of preparation, Sample 6 is presumably contaminated with sodium sulfate. The initial rapid decrease in density is due to the hydration of the salt to form the decahydrate. This then slowly goes into solution and diffuses out of the tube, causing the later slow decrease in density. A calculation based on this assumption indicated that 4.8% of sodium sulfate in the sample would account for the 21% change in density. Almquist[1a] found by analysis, 4.5% impurities, the nature of which he did not ascertain.

[5] Harkins and Ewing, THIS JOURNAL, **43,** 1787 (1921).

few days before coming to a constant density, whereas with some of the charcoals several months elapsed before the "drift" disappeared. Hulett and Harkins attribute this drift to the slowness of penetration of the liquid into the micro-pores. Our results would indicate that the micro-pores of the oxide granules constitute a much smaller proportion of the total pore volume (a conclusion borne out by results described in Part II of this paper), or else that the oxides are more easily wetted by the water than is the charcoal.

Part of the results of these determinations are summarized in Table I and shown graphically in Fig. 3. It is believed that the determinations of true density in Series 1 and 2 are precise to a few hundredths of a per cent., but that the homogeneity of the samples is not greater than a few tenths of a per cent. The pore volume and apparent density are probably not precise to much better than 2%. The results given in the tables are expressed so that the last figure given is likely to be in error by not more than 3 or 4 units.



⊙ True density, g. per cc. (use left-hand ordinates). × Pore volume, cc. per g. of solid (use right-hand ordinates). △ Apparent granule density, g. per cc. (use right-hand ordinates).

Fig. 4.

Fig. 4 shows some of the properties of Series 2, which are typical of those obtained with Series 1 and 3. The *sharp* maxima and minima shown are probably not real, but some kind of maxima and minima unquestionably exist in all three series between the composition of 50 and 70% MnO_x.

Discussion of Results.—One of the chief purposes of this investigation was to obtain an explanation of the "mixture effect" in the oxidation of carbon monoxide by gaseous oxygen as catalyzed by the oxide granules. As stated in the opening paragraphs of this paper, it was found that all of

TABLE I

CERTAIN PHYSICAL PROPERTIES OF POROUS GRANULES OF MANGANESE DIOXIDE, COPPER OXIDE AND MIXTURES OF THESE OXIDES

Sample	Tube no.	True density, g./cc.	Specific volume, cc./g.	Pore volume		Granule density, g./cc.	Apparent density, g./cc.
				cc./g. of solid	cc./cc. of solid		
Series 1 (washed)							
1	17	4.553	0.2196	0.305	1.39	1.90	(0.81)[a]
2	21	4.436	.2255	.486	2.16	1.41	.76
	22	4.433	.2256	.499	2.21	1.38	
3	23	4.561	.2192	.860	3.89	0.93	.52
4	19	4.864	.2056	.580	2.82	1.27	.68
5	18	5.260	.1901	.486	2.56	1.48	.85
6	13	5.741	.1742	.434	2.48	1.64	
	16	5.763	.1735	.434	2.50	1.65	.83
Series 2							
1	33	4.612	.2168	.456	2.10	1.49	.81
2	32	5.038	.1986	.958	4.83	0.87	.50
3	35	5.309	.1883	.805	4.27	1.01	[b]
	31	5.254	.1903	.803	4.22	1.01	.54
4	30	5.511	.1814	.568	3.13	1.33	.73
5	29	5.789	.1727	.434	2.51	1.65	.86
6	28	6.083	.1644	.374	2.28	1.86	.93
Series 3							
1		4.57	.261	.455	2.08	1.48	.72
2		3.72	.263	.633	2.69	1.01	.51
3		3.79	.258	.836	3.17	0.91	.49
4		3.87	.264	.702	2.72	1.01	.55
5		3.81	.269				.83[c]
6		3.83	.219				.94[c]
Washington samples							
1	27	4.492	.2226				.42[c]
3	26	5.092	.1964	.628	3.19	1.21	[d]
	25	5.026	.1990	.631	3.17	1.21	.65
6	24	5.986	.1671	.727	4.35	1.13	.61

[a] All of the sample was used up in the various tests so that the apparent density could not be determined; assumed to be the same density as Sample 1, Series 2.

[b] Tube 35 was prepared at the same time as Tube 31, but had stood (sealed) for three months. No great change in the condition of the granules is produced by this treatment, judging from the satisfactory check.

[c] Samples were in the form of fine powders; the pore volume could not be determined by centrifuging.

[d] This sample had been put through the density determination before, and had been allowed to stand in water for four or five weeks. The slightly increased density probably means that the granules contained a small amount of soluble impurity which was dissolved out by this treatment. Some results obtained with this sample in Part II of this paper seem to indicate the presence of soluble impurities.

the mixtures were much more active catalysts than either of the pure components alone. One of the possibilities that needed investigation was whether the two oxides on mixing formed some definite compound. Since compound formation is generally accompanied by a departure from linearity in the specific volume–composition curve, we are now in a position to apply this criterion to the present case.

Compound Formation.—The granules of Series 2 and 3 were prepared with considerably greater care than those of Series 1, both in the washing of the component oxides free from soluble salts and in the mixing of the moist oxides before drying. Sample 1 (and probably 2) of Series 1 suffered a profound chemical and physical change when they were first wetted. In the case of Series 3, results of analysis[1a] indicate that the various samples lost carbon dioxide unequally upon drying. As for the Washington samples, the three bear no relation to one another in their origin, being taken from different batches of stock oxides. Series 2, therefore, is the only complete series tested, and we are confined to a consideration of results from this series alone in drawing conclusions as to the possibility of compound formation between the oxides.

An inspection of the specific volume–composition curve for Series 2 in Fig. 3 shows that the departure from linearity is very small, the maximum departure being about 2%. This result therefore indicates that there is probably no definite compound formed between the oxides. The work of Bray and Doss[1c] furnishes additional evidence against compound formation.

Correlation of Physical Properties of Granules and their Catalytic Activity.—In attempting to find a relationship between the physical properties thus far determined and the catalytic activity, results of Series 1 must be ruled out, since the determinations of catalytic activity were made with the unwashed granules, while the results given above were made upon granules which were washed free of soluble salts. The other granules, however, are comparable.

Since Almquist's results were obtained with 5.0 cc. of granules in each case, the properties of a *fixed volume* and not of a *fixed mass* of the granules must be considered. An inspection of the results calculated on this basis fails to reveal any marked break in any of the properties between the mixtures and the pure oxides corresponding to the great difference in catalytic activity. In the case of the mixtures, rough parallelism exists between catalytic activity and pore volume for Series 2, but the parallelism fails completely in Series 3 and the entire group of samples (Series 2, 3 and the Washington samples) considered as a whole.

It would appear, therefore, that the physical properties thus far discussed bear a very minor part in determining the catalytic activity of the granules.

An explanation of the marked maxima and minima in the properties other than the specific volume is found in the colloidal character of the pastes as discussed in Part II.

Part II

With the idea that compound formation could be detected by heat effects produced on mixing these oxides in a finely divided condition, samples of MnO_x and CuO were prepared for this purpose.

The MnO_x was prepared by the Fremy method, that is, by adding potassium permanganate to a concentrated solution of sulfuric acid and allowing the permanganic acid thus formed to decompose spontaneously. The copper oxide was prepared by adding a moderately dilute solution of copper sulfate to a solution of sodium hydroxide, the latter in slight excess; both solutions were at room temperature. Upon standing, the gelatinous, blue-green precipitate of hydrated copper oxide slowly changed to brownish black. (Incidentally, it is interesting to note that a sample prepared in the same way, but with an excess of copper sulfate, has been kept for several months with no apparent change in color.) Both precipitates were washed by decantation until no trace of sulfate could be detected in the washings. The precipitates were rendered semi-colloidal by this treatment; several weeks were required for the precipitates to settle out after being stirred up. This was especially marked in the case of the copper oxide, indicating either that the copper oxide particles were smaller than the MnO_x particles, or that they were less compact (average density less), or else they had adsorbed a greater number of ions per particle upon being peptized.

Quantities of these suspensions which contained about the same amount of solid were brought together in a calorimeter and stirred by hand for about five minutes. The sensitive thermometer showed only 0.001° rise in temperature, part of which was due to stirring. Later analysis showed in a total volume of 150 cc. 2.872 g. of solid consisting of 1.175 g. of copper oxide and 1.697 g. of MnO_x (by difference). The observed heat effect corresponds to only 10 calories per mole of one of the oxides. This result furnishes strong evidence against the formation of a definite compound between the two oxides.

However, it was noticed that the precipitate settled out much more rapidly after mixing, the supernatant liquid being clear after standing overnight, although, as mentioned before, several weeks were required for the settling of the pure oxide suspensions. This result indicated that the two colloidal oxides are of opposite sign—their properties and method of formation making it probable that the copper oxide is negatively, the MnO_x positively, charged due to the adsorption of hydroxyl and hydrogen ions, respectively.

The application of the above considerations has an extremely important bearing upon the whole theory of the formation of a porous granule. Almquist and Bray[6] give the following picture of the process. The terms in italics are inserted by Draper.

"The formation of the firm, porous granule may be thought of as follows. Each hydrated oxide is precipitated in the form of minute particles, the size *and configuration* of which are determined by *the nature of the substance* and the method of precipitation, *and also by the thoroughness of washing;*

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[6] Ref. 1 a, footnote, p. 2311.

the more completely the soluble salts are removed, the finer the particles become through peptization of the precipitate. The filter cake, before it is dried, consists of particles surrounded by films of water which enable the relative positions of the particles to be easily changed, for example in a kneading process. In the preliminary drying as the water is slowly expelled, the particles are gradually drawn together, and in many places contact is sufficiently close to allow valence forces to come into play between the molecules of the different particles. The plastic material has now been transformed into a solid. Finally, as the water of hydration is gradually expelled, the body becomes porous."

Gelatinous and semi-gelatinous precipitates such as hydrated copper oxide, from the ease with which they may be peptized by washing, are thought to be composed of very small particles held together in a branching network, partly at least by the adsorbed substances on their surfaces. As such a precipitate is washed, the large flocks are progressively broken down into smaller and smaller particles, which must still be quite irregular in configuration until they approach the size of the ultimate particles which are of colloidal dimensions.

Now if a granule is formed from such a precipitate by the process given above, the pore volume (cc. per cc. of solid) will evidently be less the smaller and more regular the ultimate particles, that is, the more thoroughly the precipitate is washed. Comparison of the results for Sample 6 of Series 1 and 2 offers confirmation of this conclusion.

In the case of the pulverulent precipitates of MnO_x, the evidence given above indicates that the particles are considerably larger than the *ultimate* particles of copper oxide. As with most pulverulent precipitates, the particles are compact, rounded grains, which made a compact, dense granule. With particles which are nearly spherical, the pore volume might be expected to be nearly independent of their size,[7] but the proportion of macro-pores in the total pore volume will be less the smaller the particles.

The more irregular the particles of a given size, the larger the proportion of macro-pores might be expected to be.

From a comparison of the physical properties of the two oxides, one should expect the particles of the semi-gelatinous copper oxide in the thoroughly washed paste to be considerably smaller and considerably more irregular than the particles of the pulverulent MnO_x. Granules made from the pure copper oxide alone may therefore have a total pore volume which is greater or less than that of the granules made from the MnO_x, depending upon which of the two factors (size and irregularity)

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[7] It can be shown that the total free space in a given cube filled with close-packed spheres whose radius is small in comparison to the dimensions of the cube is independent of the radius of the spheres.

predominates. If the pore volume is approximately the same (as is the case in Series 2, Samples 1 and 6, Table I), we would predict that the proportion of cavities and macro-pores in the copper oxide granules would be greater, a prediction verified by results given later.

If our assumption as to the adsorption of ions of the opposite sign by the particles of the two oxides is correct, bringing the two pastes together will bring about peptization between the particles. This should have the effect of increasing both the size and the irregularity of the particles in the mixture. If the maximum effect is obtained in the case where the number of oppositely charged particles is the same, which appears logical since the peptization must take place particle by particle, the granule of maximum porosity should contain a large proportion of that oxide whose particles are the larger. Results given in Table I show that, from this standpoint also, the MnO_x particles are larger than those of copper oxide in Series 2. In Series 1, where the oxides were not so thoroughly washed, we find as predicted that there is less difference in the size of the oxide particles. In Series 3, the results indicate that the MnO_x particles are smaller; the copper oxide of this series was made from basic copper carbonate, which is much more pulverulent than the product made from the hydrated oxide.

It seemed desirable, in the light of the above considerations, to attempt to gain some idea as to the distribution of the pore volume between micro-capillaries, macro-capillaries and cavities in the various granules. A study of the adsorption curves for a vapor up to the saturation pressure should give us such information, since a relation can be developed connecting the vapor pressure and the curvature of the liquid surface in equilibrium with the vapor. For a liquid which wets the granules, the curvature of the liquid surface gives us a measure of the radius of the capillaries in which the liquid is condensed, and adsorption isotherms for the vapor will give the volume of all capillaries whose radius is equal to or less than that corresponding to each measured pressure. Since water had been used in determining the total pore volume, this liquid was used in determining the adsorption isotherms. A rather hasty run was made upon Sample 6 of Series 2 using ether instead of water. The isotherm had the same general shape as that for water, but the calculated value of the radius of the capillaries did not check closely for the smaller values, a result for which a number of explanations has been advanced[8,9,10,11] some assuming that the liquid in the capillaries is under relatively enormous positive or negative pressure; some that the "true adsorption"

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[8] Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

[9] Harkins and Ewing, *ibid.*, **43**, 1787 (1921).

[10] Patrick and Grimm, *ibid.*, **43**, 2144 (1921).

[11] Bachmann, *Z. angew. Chem.*, **79**, 202 (1913).

may consist of single or multiple layers of the adsorbate, depending upon the nature of the adsorbent and the adsorbate.

Since capillary condensation is preceded by "true adsorption,"[12] the calculated values for the radii of the capillaries will differ for different adsorbates if the molecular dimensions of the latter are different. This difference may be relatively great in the event that one adsorbate forms a monomolecular and the other a multimolecular adsorbed film. It is not assumed, therefore, that the radii calculated below represent the actual dimensions of the pores; it is enough for our purpose to assume that the results obtained from the various granules, with water as adsorbate, are comparable.

To calculate the effect of curvature of the liquid surface upon the vapor pressure, the following well-known formula has been derived from the rise of a liquid in a capillary. A capillary of circular cross section, the walls of which are wet by the liquid, and whose radius is so small that the liquid surface is circular is assumed in the derivation.

$$r = \rho = \frac{2\gamma M}{DRT \ln p_0/p_1} = \frac{K}{\ln p_0/p_1} \tag{1}$$

K being a constant for constant temperature. In this formula ρ = the radius of curvature of the liquid surface, r = the radius of the capillary, D = the density of the liquid, p_0 = the vapor pressure of the liquid at a plane surface, p_1 = the vapor pressure of the liquid from the concave surface, M is the molecular weight of the vapor, R = the molecular gas constant, γ = the surface tension of the liquid and ln is the logarithm to the base e.

The volume of liquid condensed in a capillary of radius r and length l, closed at one end, and where $\rho > r$, is

$$\pi r^2 l - \pi\ [2/3\ \rho^3 - \rho^2\ (\rho^2 - r^2)^{1/2} + 1/3\ (\rho^2 - r^2)^{3/2}] \tag{2}$$

Suppose that we have a system consisting of a network of capillaries threading a solid which is wet by water. If a volume, v, of water is absorbed at constant pressure, p, we know that the radius of curvature of the water surfaces in the capillaries has not changed during the absorption. If ρ is the radius of curvature of the water surface corresponding to the pressure p, the absorption is equivalent to that produced in circular cylindrical capillaries of radius ρ and total length L, where $\pi\rho^2 L = v$. The entire capillary volume of the solid can thus be represented by an aggregation of circular, cylindrical capillaries, at least as far as the volume and capillary properties are concerned. The actual shape of the pore will have a large effect upon the extent of surface exposed in the walls, but not upon the capillarity. The actual volume of water condensed in a porous body at any pressure of water vapor less than the saturation

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[12] Bray and Draper, *Proc. Nat. Acad. Sci.*, **12**, 295 (1926).

pressure will depend largely upon the *average* length of capillaries having uniform cross section rather than the *total* length of pores having this cross section, as can be seen from Equation 2.

Consider a system composed of n_1 pores of uniform radius, r_1, and average length l_1, n_2 pores of uniform radius r_2 and average length $l_2, \ldots\ldots n_k$ pores of uniform radius r_k and average length l_k. If water vapor is introduced at a pressure corresponding to a curved surface of radius ρ where $r_k < \rho < r_{k+1}$, the volume of water condensed when equilibrium is reached is evidently, from (2)

$$V = \pi\{n_1[l_1r_1^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_1^2)^{1/2} - 1/3\ (\rho^2 - r_1^2)^{3/2}] + n_2[l_2r_2^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_2^2)^{1/2} - 1/3\ (\rho^2 - r_2^2)^{3/2}] + \ldots\ldots + n_k[l_kr_k^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_k^2)^{1/2} - 1/3\ (\rho^2 - r_k^2)^{3/2}]\} \tag{3}$$

or

$$V = \pi \sum_{i=1}^{i=k} n_i[l_ir_i^2 - 2/3\ \rho^3 + \rho^2\ (\rho^2 - r_i^2)^{1/2} - 1/3\ (\rho^2 - r_i^2)^{3/2}] \tag{4}$$

If, now, $\rho = r_{k+1}$, the volume condensed at equilibrium is the same as that given in (4) plus an additive term, $\alpha\pi[n_{k+1}\, l_{k+1}\, r_{k+1}^2 - {}^2/_3\, n_{k+1}\, r_{k+1}^3]$ (5), where α is the fraction of the capillaries of radius r_{k+1} which are filled.

Differentiating (4) with respect to ρ, we obtain

$$\frac{\mathrm{d}V}{\mathrm{d}\rho} = \pi\rho \sum_{i=1}^{i=k} n_i \left[\frac{\rho^2}{(\rho^2 - r_i^2)^{1/2}} + (\rho^2 - r_i^2)^{1/2} - 2\rho\right] \tag{6}$$

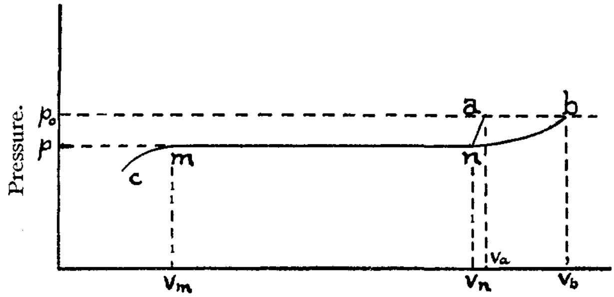
and since $\mathrm{d}V/\mathrm{d}p = (\mathrm{d}V/\mathrm{d}\rho)/(\mathrm{d}\rho/\mathrm{d}p)$, and from (1) $\mathrm{d}\rho/\mathrm{d}p = K/[p(ln\ p_0/p)^2]$

$$\frac{\mathrm{d}V}{\mathrm{d}p} = \frac{\pi K^2}{p(ln\ p_0/p)^4} \sum_{i=1}^{i=k} n_i \left\{\frac{K^2}{[K^2 - (r_i\ ln\ p_0/p)^2]^{1/2}} + [K^2 - (r_i\ ln\ p_0/p)^2]^{1/2} - 2K\right\} \tag{7}$$

An inspection of (5) tells us that any considerable volume of water condensed at constant pressure may indicate either a very large number of short capillaries of uniform radius and length, $l > {}^2/_3\ r$, or else a relatively small number of long tube-like capillaries, or anything between these extremes. Equation 7 gives some important information about the adsorption curves, as follows: the slope of the pressure–volume curve is not dependent upon the average length of the capillaries; the contribution to the slope at any given point by capillaries of any given radius is directly proportional to the number of these capillaries present. This contribution is smaller the smaller the radius of the capillary; the slope of the curve is greater (other variables being constant) the larger p becomes. (Note that when V is plotted against p as the ordinate, $\mathrm{d}V/\mathrm{d}p = 0$ indicates a vertical tangent, and $\mathrm{d}V/\mathrm{d}p = \infty$ indicates a horizontal tangent.)

The actual condition of any porous body cannot be determined from the sorption curve alone, but in some cases we can obtain a valuable comparison between porous bodies by making use of the generalizations derived from the equations just developed.

In Fig. 5, cmna and cmnb represent theoretical sorption curves for such amounts of two porous granules A and B, that the same volume of water ($v_n - v_m$) is absorbed at the same pressure p, and in which the distribution of pores of various *radii less than that corresponding to the pressure* p (r_p) *is the same* (since the branches cm coincide in the two curves). Granules A and B thus have the same total volume of pores of radius r_p. Granule A differs from Granule B in having *few pores of radius greater than* r_p, the volume $v_a - v_n$ thus representing the water necessary to fill up the menisci of a relatively *small number of capillaries*. The much larger volume $v_b - v_n$ in the curve for Granule B indicates one of two conditions: (1) *a much larger number of* capillary menisci to be filled or (2) a smaller number of capillaries of uniform radius r_p, with funnel or trumpet shaped ends.



Volume of water absorbed, cc.

Fig. 5.

The following conclusion therefore seems justified: for a given volume of liquid condensed at constant pressure, p, the more abrupt the transition from the horizontal to the high pressure branch of the sorption curve, the fewer are the capillaries of radius r_p present in the granule and, therefore, the greater is the average length of these capillaries. For a granule whose sorption curve has a long, horizontal branch with a rather abrupt transition to the high pressure branch, we are justified in assuming that there must be a rather small number of relatively long tube-like capillaries present.

Curves of type cmna were obtained by Lowry and Hulett[13] for sorption of water vapor by charcoal, in which we might expect to find a considerable number of tube-like pores.

Sorption curves were determined for Samples 1, 2, 3, 4 and 6 of Series 2 for water vapor up to saturation pressure at 25° (23.83 mm. of mercury at 45°), the results for better comparison being plotted for that weight of each sample which has a total pore volume of 1 cc. as determined in Part I. These results are shown in Fig. 6 and a typical run with calcula-

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[13] Lowry and Hulett, This Journal, **42**, 1403, Fig. 6 (1920).

tions is given in Table II. It should be noted that the form of Equation 1 is such that values of ρ become rapidly less accurate as the value of p increases. Thus, an error of 0.005 cm. of mercury in the measurement of the pressure produces the following errors in the calculated values of ρ: at p = 1.00 cm. of Hg, ρ = 12.1 Å., dρ = 0.07 Å., < 1% error; at p = 2.00 cm. of Hg, ρ = 60.0 Å., dρ = 0.86 Å., 1.4% error; p = 2.35 cm. of Hg, ρ = 755 Å., dρ = 116 Å., 15% error.

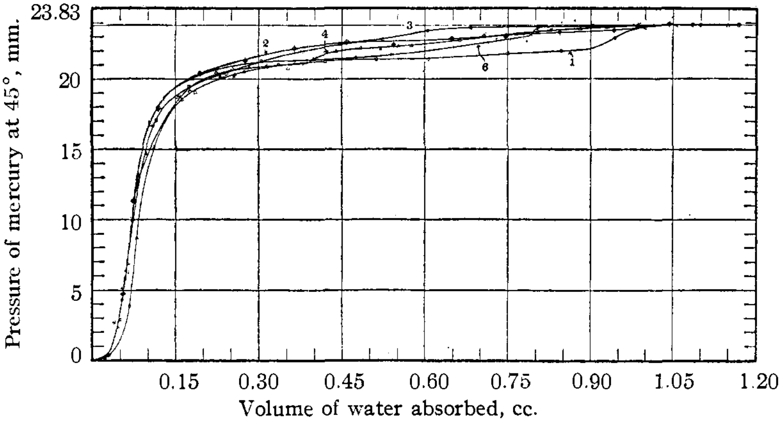

Fig. 6.

TABLE II

TYPICAL RUN ON DESORPTION CURVE FOR 0.5002 G. OF SAMPLE 2 WITH WATER VAPOR AT 25°

An excess (unmeasured) of water introduced into catalyst tube

Press. in main apparatus	Press. in catalyst tube A	Weight of water in gas phase Main app.	Weight of water in gas phase Tube A	Weight of water in gas phase Total	Weight of water in gas phase initially	Weight of water desorbed	Total weight of water desorbed	Total weight of water in granules	Volume of water in 1.245 g. of granules	$1/\rho \times 10^{-6}$ cm.$^{-1}$	$\rho \times 10^{8}$ cm.
0.042	2.386	...	0.0021	0.0021	0.0021	0.0000	0.0000	0.4973	1.0408	..	..
2.373	2.348	0.0477	.0021	.0498	.0021	.0477	.0477	.4496	0.9410	0.14	710
2.335	2.338	.0470	.0021	.0491	.0021	.0470	.0947	.4026	.8426	.18	550
2.296	2.303	.0462	.0021	.0483	.0021	.0462	.1409	.3564	.7459	.33	310
2.335	2.293	.0470	.0021	.0491	.0021	.0470	.1879	.3094	.6476	.37	270
2.273	2.245	.0457	.0020	.0477	.0021	.0456	.2335	.2538	.5312	.57	175
2.275	2.261	.0458	.0020	.0478	.0020	.0458	.2793	.2180	.4562	.50	200
2.229	2.212	.0449	.0020	.0469	.0020	.0449	.3242	.1731	.3623	.71	140
2.080	2.128	.0419	.0019	.0438	.0020	.0418	.3660	.1313	.2748	1.08	93
1.939	2.040	.0390	.0018	.0408	.0019	.0389	.4049	.0924	.1934	1.48	68
1.786	1.792	.0359	.0016	.0375	.0018	.0357	.4406	.0567	.1187	2.71	37
1.110	1.131	.0223	.0010	.0233	.0016	.0217	.4623	.0350	.0733	7.1	14
0.479	0.486	.0096	.0004	.0100	.0010	.0090	.4713	.0260	.0544	15.1	6.6
1.173	...	.0236	...	.0236	.0004	.0232	.4945	.0028	.0059	..	..
0.141	...	.0028	...	.0028	.0000	.0028	.4973	.0000	.0000	..	..

The measurements recorded in the last two lines were taken when the tube was heated to 200°. In Column 10, the volume of liquid absorbed by 1.245 g. of the granules is calculated since 1.245 g. of these granules have a pore volume of 1.00 cc.

Experimental

The sorption curves were determined by means of the apparatus shown diagrammatically in Fig. 7. All of the glass parts were made of Pyrex glass. That part of the apparatus within the dotted lines was enclosed in an automatically controlled air thermostat, the temperature of the gas in the 2-liter bulb D being maintained at 45.00 ±0.02°. After assembling, the volume of the various parts of the apparatus was carefully determined, either by adding a known amount of air and measuring the pressure change produced or by adding distilled water from a buret. The volume of the catalyst bulb A and connecting tubes to a point a on manometer B was 97.9 cc., and that of D and connecting tubes between point a on manometer B and point b on manometer E was 2233 cc.

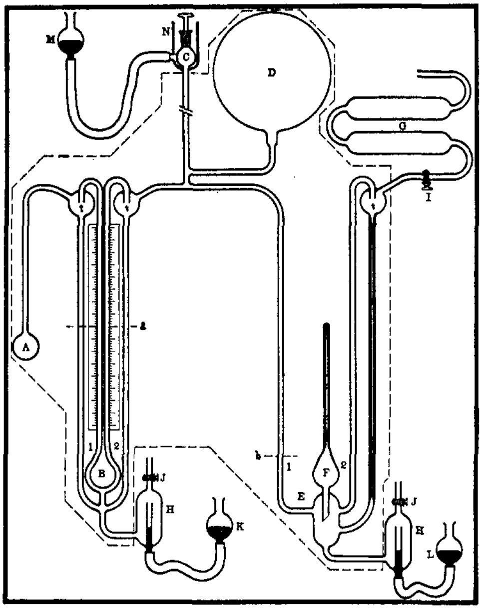

Fig. 7.

A 0.05 to 2.0 g. sample of the dried granules was placed in A, heated to 200° and evacuated through I for from three to seven hours. The small auxiliary thermostat (Fig. 8) was then adjusted to the catalyst tube and the temperature of the latter brought to 25.0 ± 0.1°, evacuation continuing until the pressure dropped to about 0.002 mm. as shown by McLeod gage F. The catalyst bulb was then cut off from the main apparatus, and the latter from the vacuum line by raising leveling bulbs K and L, respectively.

Gas-free water was then introduced into the apparatus by means of the device N, whose construction and operation have been described by Lamb and Coolidge,[8] the amount admitted being adjusted so that no vapor will condense. The amount of water present in the apparatus was then determined by measuring the pressure at manometer E, and applying the perfect gas laws. All pressures were measured by means of a cathetometer reading to 0.001 cm. Lowering K then admitted any desired amount of water into the catalyst bulb, the traps t serving to prevent any mercury from being thrown over into bulb A.

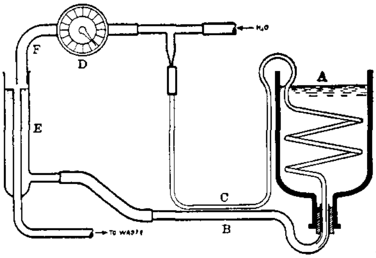

Fig. 8.

It was found simpler in practice, and the results were more reproducible when running desorption cycles. The majority of runs were made in this way. Experiments were made which demonstrated that the "zero point" could be checked to within 1% upon running an adsorption cycle, followed by a desorption cycle. It was also shown that the same curve was traced on both the adsorption and desorption cycles, no evidence of hysteresis appearing. The method of measuring the pressure probably involved the vaporization of a little of the sorbed water, so that final equilibrium may have been approached always from the same side, whether portions of water were being added or withdrawn.

The operation of the thermostat, Fig. 8, is almost self-evident from the diagram. A stream of water from the tap was passed through the tube marked "H_2O." Pinch clamp D (fitted with a dial and pointer) served to by-pass enough water through the small copper tube C to carry off just as much heat from A as entered by conduction from the air-bath.

Upon applying the principles developed from theoretical considerations to the individual curves, we arrive at the following conclusions.

Sample 1. Poorest catalyst.—A long, nearly horizontal portion of the curve with rather abrupt change near the saturation volume indicates the presence of long, tube-like pores in the granule. About 30% of the total volume sorbed is held in capillaries of radius 85 to 90 Å.; 80% is sorbed by capillaries less than 150 Å. in radius. This granule, as was predicted, is the finest grained of all those tested.

Sample 2. Most porous, second best catalyst.—Curve shows little evidence of either long, tube-like pores or large cavities. About 30% of the total volume is held in capillaries of 200 to 300 Å. radius.

Sample 3. Best catalyst.—No evidence of tube-like pores; a large number of rather large cavities. About 40% of the total volume is held in capillaries larger than 700 Å. in radius.

Sample 4.—The curve seems to give evidence of two sets of pores of nearly constant radius but rather short, one group having a radius of about 75 Å., and the other about 160 Å. This evidence is, however, rather doubtful.

Sample 6.—There is evidence, from the sharpness of the break in the curve, that there are relatively few capillaries of about 275 Å. radius and that a large number of large cavities exist in the granule. Twenty-five per cent. of the total volume is held in pores of radius greater than 300 Å. Nearly 30% of the volume is held in capillaries of radius between 75 and 110 Å. but there seems to be little evidence of tube-like pores in this range.

The generalizations that may be drawn connecting the porosity and the catalytic activity from the foregoing are:

1. The poorest catalysts are those which have the finest grained structures or, stated in another way, the poorest catalysts are those which sorb the greatest amount of water at relatively low pressures.
2. The best catalyst is one having high porosity (large total pore volume) with the smallest number of fine pores and the largest number of cavities.
3. *For the mixtures*, the slight difference in catalytic activity may be due to differences in the *accessibility* of the surface; the *mixture effect* still fails to find an explanation in the physical properties studied.

An additional result, for which it has been impossible to suggest an explanation that appears reasonable, may be pointed out at this point. In the region of "true adsorption" (vapor pressure less than half the saturation pressure) all the curves except that for Sample 1 coincide within the limits of error in the measurements. This would seem to indicate that the ratio of surface exposed to pore volume of the granules is the same for Samples 2 to 6, but is greater for Sample 1. Assuming cylindrical capillaries, their surface $S = 2\pi rl$, and their volume, $V = \pi r^2 l$, so that the ratio of surface to volume is $S/V = 2/r$, so that it would appear the material having the finest structure should have the greatest surface. Since Sample 1 has been shown by considerations enumerated above to have much the finest grained structure, it is to be expected that it should possess the largest adsorbent surface; the result that is hard to explain is that two granules which show such great differences in distribution of pore sizes as, say, Samples 3 and 6, should have the same surface.

In conclusion, I wish to express my gratitude for the help and encouragement given me by Professor W. C. Bray in the above investigation, and to my father for his assistance in making the sorption measurements.

Summary

It has been shown in the present investigation that: 1. The determination of the density of porous granules of certain oxides gave reproducible results by the immersion method of Hulett. No slow "drift" in the density of the granules similar to that encountered in determinations with charcoal was discovered. This indicates that there are few very small micro-capillaries in the former or else the resistance to filling of these pores is less. Adsorption curves prove the oxide granules to be much more coarse grained than the charcoal.

2. The porosity of the pure oxides is less than that of any of the mixtures made from them. This enhanced porosity is explained by colloidal phenomena.

3. There is no evidence of compound formation between the well washed oxides upon mixing.

4. An expression has been derived giving the volume of water sorbed by a porous body in terms of the radius of curvature of the water surface corresponding to the equilibrium pressure of the water vapor, the number and the radii and average length of the capillaries of the solid. The slope of the volume–vapor pressure curve depends upon the number and the radii of the capillaries present and the ratio of the saturation to the equilibrium pressure but not upon the average length of the capillaries. The sorption curves are shown to yield evidence as to the existence of long, tube-like capillaries in the granules in some cases.

5. Sorption curves have been determined for certain oxidation catalysts

in the form of porous granules. The poorest catalysts have the finest grained structure. No explanation for the "mixture effect" is discovered.

6. An apparent anomaly in the results has been pointed out. In the region of true adsorption, all the sorption curves except that for Sample 1 coincide, indicating nearly equal surface exposure per unit pore volume for all these granules, in spite of great difference in pore size.

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THE HEAT CAPACITY AT LOW TEMPERATURES OF ZINC OXIDE AND OF CADMIUM OXIDE[1]

BY RUSSELL W. MILLAR[2]

RECEIVED JUNE 30, 1928 PUBLISHED OCTOBER 6, 1928

Research on the heat capacities of the oxides of metals previously reported by the author[3] has been continued. For the sake of a comparison of results with those of Parks and his co-workers,[4] the heat capacity of zinc oxide was redetermined.

Materials.—The zinc oxide used was the Sample 2 described by Maier, Parks and Anderson. It had been kept in an evacuated silica flask at 1100° for sixty hours. The product was microcrystalline and contained, according to them, less than 0.1% of impurities.

The cadmium oxide used was prepared by heating pure cadmium oxide in an open platinum dish at 1100° for three days. The product was finely crystalline and of much higher apparent density than the original powder.

The values of C_p, the heat capacity in calories per mole per degree, are presented in Tables I and II and in Fig. 1 opposite the corresponding temperatures in degrees Kelvin.

The entropy was calculated, as described previously, by extrapolation to the absolute zero by means of the sum of suitable functions of the form of Debye and of Einstein. For zinc oxide a Debye function with $\beta\nu$ = 295.5 and an Einstein function with $\beta\nu$ = 753 fitted the data with an accuracy of 0.5% to 250°K., although C_v and C_p begin to deviate at much lower temperatures. At higher temperatures the experimental values fall below those given by the theoretical functions. Using C_p and log T as coördinates, the curve was extrapolated to 37.58°K., where it joined the Debye curve at $C_v = 0.860$. Below this temperature the tables of Mieth-

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[2] Associate chemist.

[3] Millar, THIS JOURNAL, **50**, 1875 (1928).

[4] (a) Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926); (b) Maier, Parks and Anderson, THIS JOURNAL, **48**, 2564 (1926).