[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Surface Areas of Porous Materials Calculated from Capillary Radii[1]

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The various means of estimating the surface areas of porous materials have occupied the attention of many investigators. Methods used include those involving diffusion of gases, heat conductivity, and adsorption isotherms. Among the last-mentioned are the highly successful calculations of Emmett and Brunauer[4] which have been applied to a large number of isotherms of gases and vapors adsorbed on a wide variety of materials. Here the gas sorbed at low pressures is considered as forming a unimolecular layer over the surface, and the area is estimated from the number and dimensions of adsorbate molecules.

Other treatments derive the surface area from pore radii obtained with the Kelvin (Thomson) equation[5] for capillary condensation. Thus Lowry and Hulett[6] and Foster[7] calculate their surface areas from the volume of condensed vapor in a cylindrical capillary of some average radius. Lowry[8] has made more accurate calculations by summing over a number of radii. Draper[9] has developed several equations to indicate the geometry of capillaries in porous catalysts.

The purpose of the present paper is to outline a method for obtaining the surface area of a large volume of pores distributed over a wide range of radii and then to apply the resulting equations to a calculation of the specific surfaces of a number of adsorbents for which adsorption data are available in the literature. In this treatment the high pressure region of an adsorption isotherm is made the basis of the surface evaluation.

Derivation.—A porous adsorbent is here considered as an assembly of many fine capillary spaces of varying sizes and shapes, which gradually fill with condensed liquid on exposure to vapors at increasing equilibrium pressures. At saturation condensed liquid occupies the whole internal volume of the porous material. The vapor pressure of liquid condensed in capillaries of given radii is presumed to obey the widely used equation of Lord Kelvin.[5] This equation is employed to convert adsorption equilibrium pressures to capillary radii; the surface evaluation to be presented depends upon the shape of curves representing volume adsorbed as a function of calculated radii.

Although the Kelvin expression could be applied to any adsorption isotherm, it is probable that only those which are sigmoid in shape involve pores which account for a substantial part of the total volume of adsorbed vapor. Sorption at pressures so low as to correspond, according to the Kelvin equation, to radii of but one or two molecular dimensions is usually attributed to surface adsorption rather than to capillary condensation. Condensation in capillaries is considered in this paper as restricted to that portion of an S-shaped isotherm which is convex to the pressure axis. It is in this region that many adsorbents give isotherms with hysteresis loops; and hysteresis of the magnitude usually observed has been generally regarded as evidence of porosity.

In deriving the total surface area of a porous adsorbent from capillary radii and volumes adsorbed, four further assumptions have been made: 1, the surface represented by the walls of capillaries constitutes practically the entire surface of the adsorbent and far exceeds its external surface; 2, pores fill in the order of their increasing size and empty in the reverse order; 3, since some shape must be assumed, the pores are regarded as cylindrical; and 4, there is "complete wetting" of the capillaries by adsorbate.

For the ideal case of an adsorbent containing cylindrical pores all of the same radius, r, the surface area would be simply $2V/r$, where V is the volume of liquid adsorbed during capillary condensation. This ideal case still remains to be reported for an actual adsorbent. However, an idea as to the distribution of capillaries may be obtained from the volume–radius curves already mentioned. Such curves for most systems can be divided into two or three straight-line portions, each portion representing a capillary distribution with the total (integral) volume adsorbed approximately proportional to the capillary radius over a wide range of radii. Occasionally one such relationship holds for the entire range of capillary sizes; often when two or three portions are required, no approximation to a straight line is entirely satisfactory in the region of largest radii. Fortunately, poor approximations in this region affect only slightly the specific surface areas of actual adsorbents obtained by the method to be described.

An integrated volume–radius relationship may be calculated by plotting radius against length of successively wider capillaries and revolving this

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[4] See P. H. Emmett in "Advances in Colloid Science," edited by E. O. Kraemer, Interscience Publishers, Inc., New York, N. Y., 1942, pp. 1–36.

[5] J. W. McBain, "The Sorption of Gases and Vapours by Solids," G. Routledge and Sons, Ltd., London, 1932, pp. 432–433.

[6] H. H. Lowry and G. A. Hulett, THIS JOURNAL, **42**, 1393 (1920).

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[8] H. H. Lowry, THIS JOURNAL, **46**, 824 (1924).

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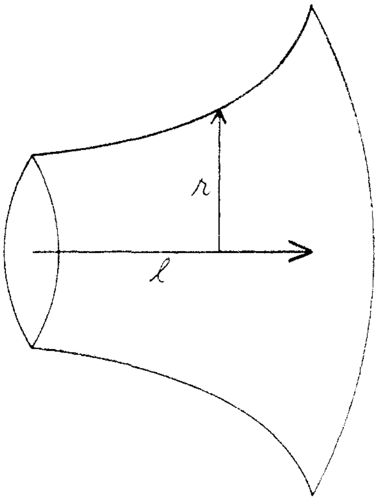

Fig. 1.

curve through 360°. This leads to the horn-shaped figure shown in Fig. 1, for which the volume of an infinitesimal section, dV, is

$$\mathrm{d}V = \pi r^2 \mathrm{d}l \qquad (1)$$

Furthermore, according to the calculus, the following general relation exists between S (surface), r, and l (length) of a volume of revolution:

$$S = 2\pi \int_{l_1}^{l_2} r\sqrt{1 + (\mathrm{d}r/\mathrm{d}l)^2}\,\mathrm{d}l \qquad (2)$$

Since nothing is known about l, the length of a capillary, S must be found in terms of dV and dr. Because V (volume of adsorbate) is taken as proportional to capillary radius, r, it follows that

$$\mathrm{d}V = k\mathrm{d}r \qquad (3)$$

where k is, of course, the slope of the line obtained when V is plotted against r. Substitution of kdr for dV in Eq. 1, followed by substitution of $k\mathrm{d}r/\pi r^2$ for dl in Eq. 2, gives

$$S = 2k \int_{r_1}^{r_2} \sqrt{1 + (\pi r^2/k)^2}\,\mathrm{d}r/r \qquad (4)$$

Integration by substitution leads directly to

$$S = k\left[\sqrt{1 + (\pi r^2/k)^2} - \ln\frac{1 + \sqrt{1 + (\pi r^2/k)^2}}{\pi r^2/k}\right]_{r_1}^{r_2}$$

Because k is very large, the volume being measured in cc. and r in 10^{-8} cm., this expression reduces to

$$S = k\left[1 - \ln(2k/\pi r^2)\right]_{r_1}^{r_2}$$

The equation can be simplified because evaluations are made over a particular radius range (r_1 to r_2) for which $V = kr$ is valid. Transformation to base 10 logarithms leads to

$$\Delta S = 4.607(V_2 - V_1)(\log r_2/r_1)/(r_2 - r_1) \qquad (5)$$

where ΔS is the surface area of all capillaries with radii between r_1 and r_2.

Equation 5 could now be applied to the calculation of surface areas. However, before proceeding with calculations, one of the assumptions made in the derivation deserves critical examination. It was assumed that the capillaries were completely empty before condensation and that any volume of vapor, added or removed, completely filled or emptied the capillary of the next size. Such an assumption contradicts the current belief of sorption chemistry that a unimolecular layer is formed over most, if not all, of the surface of an adsorbent before capillary condensation sets in, and therefore Eq. 5 will be in error by an amount corresponding to the adsorbed layer. But the surface area calculated will be little affected by the presence of this layer when most of the capillaries in a given material are large in comparison with the diameter of a molecule.

An exact correction for the volume of liquid condensed on the capillary walls could have been applied by plotting r originally against V multiplied by an appropriate function to include the adsorbed layer. This complicated procedure may be avoided by correcting the derived surface at the present stage, if a correction is deemed necessary. An approximate correction may be made by substituting a cylinder with the same surface and volume for the horn-shaped figure representing Eq. 5 for a particular ΔV and ΔS. The characteristic radius, r^*, of this single cylindrical capillary is, then

$$r^* = 2\Delta V/\Delta S = (r_2 - r_1)/2.303\,(\log r_2/r_1)$$

This cylinder with radius r^* may be regarded as composed of two concentric cylinders, the larger one including the adsorbed layer, and the smaller with radius $r^* - d$ (where d is the thickness of the adsorbed layer), excluding it. If the radii obtained with the Kelvin equation correspond to the radius of the outer cylinder, r^*, while the volume ΔV of Eq. 5 is the volume of the inner cylinder, the corrected volume necessary to fill completely the outer cylinder, that is, the capillaries with radii between r_1 and r_2, is

$$(r^*)^2(V_2 - V_1)/(r^* - d)^2$$

where d is the diameter (or thickness) of an adsorbed molecule. Hence, Eq. 5 corrected for this factor becomes[9a]

$$\Delta S^* = \frac{(r^*)^2}{(r^* - d)^2}\,4.607\,\frac{(V_2 - V_1)}{(r_2 - r_1)}\log\frac{r_2}{r_1} \qquad (6)$$

[9a] Since this method of correction favors the larger capillaries, for which the thickness of the adsorbed layer is relatively less important than for the smaller ones contributing to a particular $V = kr$, the surface areas corrected according to Eq. 6 will be somewhat low. A more exact procedure for taking the adsorbed layer into consideration would be to substitute $r - d$ for r in Eqs. 1 and 2, and to obtain an equation analogous to 5, but with the adsorbed layer altogether omitted. With this procedure, the correction factor would depend on the ratio of radii including and excluding the thickness of the adsorbed layer, rather than on the ratio of these terms squared. The final corrected surface equation, analogous to Eq. 6, would be

$$\Delta S^*_{\mathrm{a}} = \frac{R^*}{R^* - d}\,4.607\,\frac{V_2 - V_1}{r_2 - r_1}\log\frac{r_2 - d}{r_1 - d} \qquad (6a)$$

where

$$R^* = \frac{r_2 - r_1}{2.303\log\dfrac{r_2 - d}{r_1 - d}}$$

TABLE I

SPECIFIC SURFACES OF ADSORBENTS

		Total surface (sq. m./g.) calcd. from				
		Capillary radii				
System	Ref.	Adspn.	Desorp.	Eq.	Mol. diam., Å.	Point B
Silica aerogel–butane (0°)	11	547	650	5	...	248[a]
Silica aerogel–nitrogen (−183°)	11	...	...	..	...	707[b]
Silica aerogel–butane (0°)	11	607	722	6	5.0	248[a]
Water-aged aerogel–butane (0°)	11	271	314	5	...	123[e]
Water-aged aerogel–butane (0°)	11	300	342	6	5.0	123[e]
Silica gel I–water (60°)	12	79.8	...	6	3.5	...
Silica gel I–ethanol (60°)	12	...	...	..	...	380
Silica gel II–water (15°)	13	312	372	5	...	...
Silica gel II–ethanol (15°)	13	...	...	..	...	593
Silica gel II–water (15°)	13	438	557	6	3.5	...
Silica gel II–benzene (15°)	13	270	301	5	...	490
Silica gel II–benzene (15°)	13	438	525	6	4.8	490
Titania gel–ammonia	14	...	177[c]	5	...	325
Titania gel–ammonia	14	...	297[c]	6	3.5	325
Titania gel–carbon tetrachloride (0°)	15	109	...	5	...	310
Titania–carbon tetrachloride (0°)	15	221	315	6	6.0	310
Titania gel–benzene (20°)	15	118	...	5	...	412
Titania gel–benzene (20°)	15	214	...	6	4.8	412
800° heated titania–benzene (0°)	15	20.6	35.4	5	...	29
Heated titania gel–benzene (0°)	15	23.9	43.9	6	4.8	29
Ferric oxide gel–ethanol	16	102	123	5	...	211
Ferric oxide gel–ethanol	16	179	245	6	5.2	211
Water-aged ferric oxide–ethanol	16	32.1	39.0	5	...	52
Water-aged ferric oxide–ethanol	16	36.2	45.8	6	5.2	52
Copper-manganese oxides–water	9	158[c]	...	6	3.5	200
Charcoal–water (100°)	17	450[c]	...	5	...	...
Charcoal–carbon disulfide (59°)	17	...	...	..	...	914
English charcoal–water	6	418[c]	...	6	3.5	...[d]

[a] Surface of 393 sq. m./g. from equation using v_m.[4] [b] Surface of 690 sq. m./g. from equation using v_m.[4] [c] May be adsorption instead of desorption isotherm, or *vice versa*. [d] Surface of 300 sq. m./g. by Hulett's capillary method.[6] [e] Surface of 186 sq. m./g. from equation using v_m.[4]

A number of calculations for representative adsorbents have been collected in Table I. Surface areas from capillary radii have been calculated with Eq. 5 or 6 or with both. In addition, surface areas have been obtained by Emmett and Brunauer's "Point B" method,[4] using areas covered by molecules in the liquid state (density data from "International Critical Tables," Vol. III) and locating "Point B" according to their directions. This method was used rather than the complete expression for v_m[4] because of its simplicity and because sufficient data in the literature were not always available to calculate v_m. The molecular diameters (for use in Eq. 6) and other necessary physical quantities, such as used to calculate capillary radii, were derived chiefly from values in the "International Critical Tables." Benzene was considered as a "pancake" on the surface and its thickness obtained from data given by Pauling.[10] When hysteresis was present, its start was taken as the beginning of capillary condensation and the surface calculated from the remainder of the adsorption (or desorption) isotherm to saturation. Hysteresis was absent from the last four systems in Table I. In these cases the calculation was made for radii of about one and one-half molecular diameters and upwards.

Discussion

The surface areas obtained by the capillary radius method are shown in Table I to be in the majority of cases in at least fair agreement with those determined by Emmett and Brunauer's "Point B" method.[4] The agreement appears best when Eq. 6 is applied to the desorption isotherm in using the capillary radius method. Indeed, with hysteresis present, the desorption isotherm has usually been considered as most nearly reflecting true equilibrium conditions within the adsorbent. Surface values from capillary radii and from "Point B" would be expected to ap-

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proach one another closely when each method is operating under optimum conditions. Such conditions obtain when the adsorption isotherm undergoes a sharp change at a low pressure to give a well-defined "Point B" and when capillary condensation sets in at a fairly high pressure well separated from "Point B"; this is illustrated by Lambert and Foster's water-aged ferric oxide–ethyl alcohol system.[16]

The results in the table indicate that, for the most part, the adsorbents chosen for application of the equations satisfactorily fulfill the requirements of one of the original assumptions, namely, that the surface represented by the walls of capillaries constitutes practically the entire surface of the adsorbent. Otherwise, surface values from capillary radii probably would have been consistently lower than those from unimolecular adsorption.

Agreement with the surface area values from "Point B" in the case of Lambert and Foster's silica gel[12] leaves much to be desired. Since hysteresis with water occurs in this gel in capillaries of from 10.45 to 19.23 Å. radius and since these small capillaries account for only 0.0565 g. of the 0.22 g. total liquid adsorbed, the discrepancy is probably due, in part at least, to neglecting very small capillaries which contribute a large surface area. It is interesting to note that benzene and ethyl alcohol, molecules larger than water, showed no hysteresis when adsorbed on this gel. Presumably after the surface had been covered little further room remained for capillary condensation.

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Summary

Equations have been developed which permit relatively easy calculation of the surface areas of porous adsorbents from the high pressure portion of adsorption isotherms. When the adsorbed layer is taken into consideration and when the desorption isotherm is used, pore radii usually give surface areas in good agreement with those obtained by the "Point B" method of Emmett and Braunauer. A tabulation of results by both methods is included for representative vapor–adsorbent systems.

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Factors Affecting the Precipitation of Some Insoluble Quinaldates

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Introduction

In the several publications dealing with the use of quinaldic acid (quinoline-2-carboxylic acid) as a precipitant for inorganic ions, considerable attention is given to securing the correct hydrogen ion concentration for precipitation of a given ion, or for its separation from some other ion or ions. The original investigations[1,2] on the use of quinaldic acid dealt mainly with the determination of copper, zinc and cadmium, and the separation of the former two ions from others whose quinaldates under the same conditions were more soluble. Later work by Shennan[3,4] and by Majundar[5] established more precisely some conditions for the precipitation of copper and cadmium, although agreement regarding the exact conditions for separating these ions was not reached.

Considerable work has been done in the field of organic precipitants concerning the effect of *p*H on their mode of action and, while this type of data has been applicable in special cases, it has not been amenable to a more general treatment.

It would appear that the precipitation of a metallic ion by an organic compound (when salt formation is involved) should not differ fundamentally, at least in theory, from the precipitation of, for example, a metallic sulfide. That is, the point of initial precipitation should depend upon (1) the concentration of metallic ion, (2) the concentration of precipitant, and (3) the *p*H. The solubility of the metallo-organic complex, once formed, will depend upon the excess of precipitant and the *p*H of the solution. With data showing the effect of these factors on the quantity of an ion precipitated, it becomes possible to calculate solubility products for the insoluble complexes. Then, using these, it is possible to make useful predictions concerning the behavior of any quantity of metallic ion (or ions) under any of the variable conditions.

We have attempted to collect information of this sort for several of the insoluble quinaldates, particularly the copper, cadmium and zinc salts which are of analytical interest. The line of attack has been as follows: for given concentrations of metallic ion and precipitant, the fraction precipitated has been determined as accurately as possible. Solubility products, and practical applications, have been derived from these data.

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