radius sum for Si and C is 1.94 Å., or 1.88 Å. if an empirical correction is made for the electronegativity difference; but neither of these values can be correlated with the several Si–C distances observed. If the repulsion between Cl and CH_3 both attached to a silicon atom were less than between two methyl groups, the decrease in the Si–C length when two chlorines are substituted in $Si(CH_3)_4$ could be accounted for. In that case, however, an increase in the Si–Cl distance and a decrease in the Cl–Si–Cl angle would be expected in $Si(CH_3)_2Cl_2$ as compared with $SiCl_4$; this is not observed.

Summary

Electron diffraction measurements have been made on the vapors of dimethyl silicon dichloride, methyl silicon trichloride and trifluoro silicon chloride with the results shown in Table VI.

The observed Si–C distance is shorter than in $Si(CH_3)_4$, while the Si–Cl distances are not much different from the values observed in other silicon chlorides. The SiF_3 group in SiF_3Cl does not bind the chlorine more tightly than in $SiCl_4$ in contrast to the effect observed in CF_3Cl compared with CCl_4.

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[CONTRIBUTION FOR THE CONTINENTAL CARBON COMPANY]

Hysteresis and the Capillary Theory of Adsorption of Vapors[1]

BY LEONARD H. COHAN

Introduction

The Zsigmondy capillary theory[1a–6] was one of the earliest of the theories[7–13] which have been proposed to explain the adsorption of vapors on solids. It will be the purpose of this paper to reëxamine, in the light of recent experiments, how satisfactory an explanation this theory offers.

The Zsigmondy capillary theory is based on the Kelvin equation

$$P = P_0 e^{-2\sigma V\cos\theta/r_c RT} \qquad (1)$$

which relates r_c, the radius of a capillary, to P, the pressure of a vapor in equilibrium with liquid condensed in the capillary. P_0 is the normal saturation vapor pressure of the liquid at the temperature T; σ and V are, respectively, the surface tension and molal volume of the liquid; and θ is the angle of contact between the surface of the liquid and the walls of the capillary. If the liquid wets the walls of the capillary completely, $\Theta = 0°$ and $\cos\Theta$ is one and drops out of the equation.

Due to the presence of capillary pores of varying radii, a solid can hold a condensed liquid at vapor pressures below the normal condensation pressure. The distribution of pore sizes in the solid will determine the amount of liquid held at any vapor pressure, *i. e.*, it will determine the adsorption isotherm. Objections to this theory are, first, the difficulty of explaining adsorption results at low relative pressures which in some cases[14] require r_c to be smaller than the diameter of the adsorbed molecule; and, second, the scarcity of quantitative predictions which could be tested experimentally.

Some investigators have reasoned that the first objection is not critical because σ and V of equation (1) might be much larger for liquids in small capillaries than for the same liquids in bulk. If this were the case P/P_0 might reach very low values even in capillaries where r_c is much larger than molecular dimensions. Shereshefsky[15] determined the rate of evaporation from capillaries only 2 μ in radius. From the rate of evaporation, $\Delta P = P - P_0$ was calculated and found to be about eight times that predicted by equation (1). On this basis, there would be but little difficulty in ascribing adsorption at low relative pressures to condensation in capillaries. However, the usefulness of equation (1) as an aid in determining the structure of sorbents would largely disappear since σ and V would have to be known as a function of r_c before pore radius distribution could be calculated from adsorption isotherms.

More recently, Cohan and Meyer[16] determined σ and V in capillaries 2 μ in radius and found no deviation from normal values for the liquids used by Shereshefsky. In view of these results, Shereshefsky's experiments cannot be considered a serious limitation to the usefulness of equation

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(1) Original manuscript received September 18, 1941.

(1a) Lord Kelvin, *Proc. Roy. Soc., Edinburgh*, **7**, 63–68 (1870).

(2) R. Zsigmondy, *Z. anorg. Chem.*, **71**, 356–377 (1911).

(3) W. Bachmann, *ibid.*, **73**, 125–172 (1912).

(4) R. Zsigmondy, W. Bachmann and E. F. Stevenson, *ibid.*, **75**, 189–197 (1912).

(5) J. S. Anderson, *Z. physik. Chem.*, **88**, 191–288 (1914).

(6) W. A. Patrick and J. McGavack, THIS JOURNAL, **42**, 946–978 (1920).

(7) A. Eucken, *Verhandl. deut. physik. Ges.*, **13**, 345–352 (1914).

(8) M. Polanyi, *Z. Elektrochem.*, **26**, 370–377 (1920).

(9) I. Langmuir, THIS JOURNAL, **38**, 2221–2295 (1916); **40**, 1361–1403 (1918).

(10) J. H. DeBoer and C. Zwicker, *Z. physik. Chem.*, **B3**, 407–418 (1929).

(11) R. S. Bradley, *J. Chem. Soc.*, 1467–1474 (1936); 1799–1804 (1936).

(12) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309–319 (1938).

(13) S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, *ibid.*, **62**, 1723–1732 (1940).

(14) A. G. Foster, *Trans. Faraday Soc.*, **28**, 645–657 (1932), also ref. 10, p. 1800, and ref. 6, p. 973.

(15) J. L. Shereshefsky, THIS JOURNAL, **50**, 2966–2985 (1928).

(16) L. H. Cohan and G. E. Meyer, *ibid.*, **62**, 2715–2716 (1940).

(1) in the study of sorbent structure, neither, on the other hand, can they help to eliminate our first objection to the Zsigmondy capillary theory. One must conclude that the capillary theory can only be applied to vapor adsorption provided we consider that an adsorbed layer is formed on the surface of the sorbent before capillary condensation begins.

Evidence will be presented in this paper to show that a great many experimental results can be explained if we assume that the mechanism of adsorption on a porous solid consists in the formation of a monomolecular layer followed by capillary condensation. In the following, this mechanism will be referred to simply as the capillary theory. While such a model is too simple to be more than a first approximation, a considerable amount of experimental data can be correlated. It will also be shown in a subsequent paper that fairly accurate surface area values can be determined on the basis of this hypothesis.

The above mechanism is free from the first objection to the Zsigmondy capillary theory at least in so far as the necessity for considering pores smaller than molecular dimensions is concerned. There may still be some difficulty in visualizing the application of the concepts on which equation (1) is based, such as surface tension and angle of wetting to capillaries of a few molecular diameters in radius. Nevertheless, the results reported in this paper indicate that a relation of the same form as equation (1) in which σ and V are approximately equal to the normal surface tension and molar volume and $\cos \Theta = 1$, appears to hold for capillaries whose radius is only twice the diameter of the sorbate molecule.

Turning now to the second objection, the only prediction that has been made on the basis of the Zsigmondy capillary theory is that at relative pressures equivalent to equal values of r_c as calculated from equation (1), the volume of liquid adsorbed should be constant for all sorbates and should be independent of the temperature. In some systems, this has been found to be the case, but discrepancies have occurred.[5,6,14,19] In fact, considering the capillary theory mechanism given above, the volumes need be strictly constant only if monomolecular adsorption is negligible compared to capillary condensation. Other predictions are, however, possible on the basis of the capillary theory. As will be shown below, these predictions are in good agreement with experimental data.

In the light of the foregoing discussion, reconsideration of the capillary theory certainly appears in order. This is all the more true since the capillary theory is the only adsorption theory which at present can offer an explanation for sorption hysteresis in rigid gels. The importance of such an explanation has been greatly increased by recent work[17,18] which demonstrate that hysteresis is a reproducible phenomenon and is not, as thought by previous workers,[19,20,21] merely due to the presence of gases in the apparatus or to failure to obtain true equilibrium.

Theories of Hysteresis

Three explanations, all based on the capillary theory of adsorption, have been advanced to explain hysteresis in rigid sorbents.[22]

1 **Incomplete Wetting Theory.**[2,6]—Hysteresis is due to θ of equation (1) being greater during adsorption than during desorption probably due to the presence of permanent gases. In favor of this theory is the fact that in some systems[23-26] it has been found possible to eliminate hysteresis by the painstaking removal of permanent gases. However, the sharply reproducible results of Rao and Higuti can hardly be explained in this way.[27]

2. **Bottle Neck Theory.**[28,29]—For a pore having a narrow neck of radius, r_n, and a wider body of radius, r_b, adsorption occurs in accordance with equation (1) with $r_c = r_b$. Once the pore is filled, provided no break in the liquid column occurs, desorption cannot take place until the pressure falls to the value corresponding to equation (1) with $r_c = r_n$ and, therefore, hysteresis occurs.

(17) K. S. Rao, *J. Phys. Chem.*, **45**, 500–538 (1941).

(18) I. Higuti, *Bull. Inst. Phys. Chem. Research* (Tokyo), **18**, 657–684 (1939); **19**, 951–975 (1940); **20**, 130–136 (1941).

(19) B. Gustaver, *Kolloidchem. Beihefte*, **15**, 185–338 (1922).

(20) J. R. Katz, *Proc. Acad. Sci. Amsterdam*, **26**, 548–560 (1923).

(21) A. S. Coolidge, THIS JOURNAL, **46**, 596–627 (1924), p. 600; also ref. 6, p. 961–977.

(22) The theories of W. W. Barkas, *Trans. Faraday Soc.*, **38**, 194–209 (1942); R. S. Bradley, *J. Chem. Soc.*, 1798–1804 (1936), p. 1801; A. R. Urquhart, *J. Textile Inst.*, **20**, 125–32T (1929); A. E. Benton and T. S. White, *ibid.*, **53**, 2807–2808 and 3301–3314 (1931); G. H. Piper, *Trans. Faraday Soc.*, **29**, 538–543 (1933); C. O. Seborg and A. J. Stamm, *Ind. Eng. Chem.*, **23**, 1271–1275 (1931); and M. Gordon, I. Lavine and L. C. Harrington, *ibid.*, **24**, 928–932 (1932). would apply only to non-rigid systems. The theory of B. Von Il'in, *Z. physik. Chem.*, **A155**, 403–416 (1931), is a mathematical statement of the observed facts for a given isotherm and not a mechanism on the basis of which general predictions can be made. The hypothesis of H. Engelhard and W. Stiller, *Z. Elektrochem.*, **40**, 833–836 (1934), does not apply to a system which has reached equilibrium. The explanation proposed by A. G. Foster, *Proc. Roy. Soc. Edinburgh*, **A146**, 129–140 (1934), and also by A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **15**, 433–42T (1924), p. 440, is a qualitative statement similar to the quantitative deductions of the third theory discussed in the text.

(23) S. J. Gregg, *J. Chem. Soc.*, 1494–1512 (1927).

(24) W. A. Patrick and J. McGavack, ref. 6, p. 961–967.

(25) R. Fricke and H. Marquhardt, *Kolloid-Z.*, **60**, 124–129 (1932).

(26) H. A. Hamm and W. A. Patrick, *Textile Research*, **6**, 401–409 (1936).

(27) The bulk of the evidence in the literature indicates that in systems containing permanent gases hysteresis extends over the entire isotherm while hysteresis observed in the absence of permanent gases extends only over a limited portion of the isotherm. Thus there appears to be at least two phenomena involved; namely, unlimited hysteresis which can be in part explained by this theory and limited hysteresis which cannot. It is only the latter type (see Fig. 3) in which we are interested in this paper.

(28) E. O. Kraemer, "A Treatise on Physical Chemistry," edited by H. S. Taylor, D. Van Nostrand Co., New York, N. Y., 1931, Chap. XX, p. 1661.

(29) J. W. McBain, THIS JOURNAL, **57**, 699–700 (1935).

3. **Open Pore Theory.**—In the case of a pore open at both ends, liquid cannot condense at the equilibrium vapor pressure given by equation (1) because a meniscus cannot form. As previously shown,[30] the pressure, P_a, at which the meniscus forms depends on the radius of curvature, r, of the cylindrical film on the wall of the capillary, that is

$$P_a = P_0e^{-\sigma V/rRT} = P_0e^{-\sigma V/(r_c-D)RT} \qquad (2)$$

where r_c is the radius of the pore and D the thickness of the adsorbed film which according to the capillary theory would be monomolecular; *i. e.*, D would be the height of a sorbate molecule in a direction perpendicular to the surface.[31]

Once condensation has occurred a meniscus is present and the pressure, P_d, at which evaporation occurs is given by equation (1).[32] Assuming that wetting is complete, $\cos\theta = 1$ and

$$P_d = P_0e^{-2\sigma V/r_cRT} \qquad (3)$$

Some objection has been offered to the open pore theory because the theory as originally stated applied only to pores open at both ends, a type of structure which would not be expected to occur very commonly.[33] In this connection it is important to point out that the above considerations also apply to closed capillaries possessing constrictions. Such constrictions could be of the hour-glass type or merely the upper portion of a cavity. For example, in the cavity depicted in Fig. 1 a meniscus cannot form in the upper portion of the cavity until the lower of the two pressures $P_{a_1} = P_0e^{-2\sigma V/r_vRT}$ or $P_{a_2} = P_0e^{-\sigma v/(r_s-D)RT}$ is reached. P_{a_1} corresponds of course to the pressure at which the meniscus finally reaches the widest part of the cavity at r_v and P_{a_2} corresponds to the pressure in equilibrium with the cylindrical film at the smallest radius, r_s, of the upper half of the cavity. Thus P_a equals the lower of P_{a_1} or P_{a_2} and P_d is given by equation (3). For P_{a_1} equal to or less than P_{a_2} hysteresis will only occur in accordance with the bottle neck theory. However, for P_{a_2} less than P_{a_1} hysteresis will occur in accordance with the open pore theory.

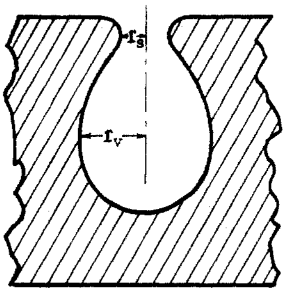

Fig. 1.

Based on the open pore theory, and, hence, on the capillary theory, two important predictions can be made. The first concerns the point on the isotherm at which hysteresis begins, and the second, the relation between adsorption and desorption pressures obtained on scanning the hysteresis loop.

Point of Hysteresis Inception

Considering equations (2) and (3), it is seen that for $r_c > 2D$, P_a is greater than P_d and hysteresis results but that for $r_c = 2D$

$$P_a = P_d = P_0e^{-\sigma V/(r_c-D)RT} \qquad (4)$$

and no hysteresis occurs.[34] Thus if sufficiently small open or constricted capillaries are present the pressure, P_h, at which hysteresis begins should correspond to the equilibrium pressure for $r_c = 2D$. From equation (4)

$$P_h = P_0e^{-\sigma V/DRT} \qquad (5)$$

or

$$D = \frac{-\sigma M}{dRT\ln P_h/P_0} \qquad (6)$$

where M is the molecular weight of the sorbate and d the density.

In Table I the values of D calculated by means of equation (6) from experimentally determined values for P_h are compared with D_{cubic} calculated for the sorbate in question from the expression $(M/Nd)^{1/3}$ and $D_{\text{spherical}}$ calculated from the molecular weight and density of the sorbate assuming spherical molecules and hexagonal close packing in the normal liquid. Except where otherwise indicated, room temperature was used. All available experimental evidence applying to hysteresis of the limited type in rigid sorbents has been included. However, it is felt that the greatest weight should be attached to the results of Higuti as in this series of experiments the point of hysteresis inception was specifically investigated for a great many sorbates on the same sorbent.

The author's value for P_h for water on silica gel was obtained at 28 ± 0.2°. The isotherm

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[30] L. H. Cohan, *ibid.*, **60**, 433-435 (1938).

[31] In reference 30, it was assumed that D was negligible compared to r_c and therefore $r_c = r$. For the purposes of the present work, this assumption is not justified.

[32] Since an adsorbed layer of thickness D forms prior to capillary condensation and is more stable than the condensed liquid there is some argument for assuming that the curvature of the meniscus is independent of this adsorbed layer and therefore $r_c - D$ should be substituted for r_c in equation (1). If this assumption is made hysteresis would occur whenever capillary condensation in open pores occurs and the limited nature of hysteresis would then have to be explained by the fact that surface adsorption or capillary adsorption in wedge shaped pores is entirely responsible for adsorption below the hysteresis region. This in itself is perfectly plausible; however, the equation that would arise in place of equation (7) below is not in as good agreement with experimental results. Furthermore, as will be shown in a later paper, surface area values determined on the basis of this theory would not be in as good agreement with other methods. For these reasons, we will assume for the present that the curvature of the meniscus is not independent of the adsorbed layer and that equation (1) applies.

[33] P. H. Emmett and Thomas W. DeWitt, THIS JOURNAL, **64**, 1253-1262 (1942).

[34] If $r_c < 2D$ adsorption and desorption occur at the same pressure regardless of whether the sorbate is held by surface adsorption or capillary condensation. If capillary condensation is assumed to take place in pores of this size adsorption would occur at P_a given by equation (4). Likewise desorption must also occur at this same pressure since a comparison of equation (3) with equation (4) shows that the pressure calculated by means of equation (3) is actually higher than P_a. That is, the vapor pressure of the cylindrical film is less than for the spherical meniscus and equation (3) cannot apply to capillary condensation in this case.

for this system appears in Fig. 2. The reversible hysteresis region is bounded by the desorption and resorption curves (heavy lines).[35] Although insufficient points were taken in the region of hysteresis inception, the true inception point cannot be far from that indicated in the figure.

TABLE I

Sorbent	Sorbate	D cubic, Å.	D spherical, Å.	D, Å., calcd. from Eq. 6	Investigator
TiO_2 gel	C_6H_6	5.3	5.9	6.1	Higuti[18]
TiO_2 gel	C_6H_5Cl	5.5	6.2	5.8	Higuti[18]
TiO_2 gel	$C_6H_5CH_3$	5.6	6.3	5.9	Higuti[18]
TiO_2 gel	CH_3OH	4.1	4.6	6.2	Higuti[18]
TiO_2 gel	C_2H_5OH	4.6	5.2	6.2	Higuti[11]
TiO_2 gel	n-C_3H_7OH	5.0	5.6	6.2	Higuti[11]
TiO_2 gel	i-C_3H_7OH	5.0	5.6	6.3	Higuti[18]
TiO_2 gel	n-C_6H_{14}	6.0	6.8	7.1	Higuti[18]
TiO_2 gel	n-C_7H_{16}	6.2	7.0	7.2	Higuti[18]
TiO_2 gel	$CH_3COOC_2H_5$	5.4	6.1	6.6	Higuti[18]
TiO_2 gel	CCl_4	5.4	6.1	6.3	Higuti[18]
TiO_2 gel	$CHCl_3$	5.1	5.8	6.3	Higuti[18]
TiO_2 gel	CH_2Cl_2	4.7	5.3	5.2	Higuti[18]
TiO_2 gel	$(C_2H_5)_2O$	5.5	6.2	6.8	Higuti[18]
TiO_2 gel	CS_2	4.6	5.2	5.6	Higuti[18]
TiO_2 gel	H_2O	3.1	3.5	4.4	Higuti[18]
TiO_2 gel	NH_3	3.2	3.6	4.3	Higuti[18]
TiO_2 gel	SO_2	3.8	4.3	5.9	Higuti[18]
SiO_2 gel	H_2O	3.1	3.5	4.3	Cohan
SiO_2 gel B	C_2H_5OH	4.6	5.2	6.6	Foster[36]
SiO_2 gel B	CH_3OH	4.1	4.6	7.6	Foster[36]
SiO_2 gel B	n-C_3H_7OH	5.0	5.6	6.1	Foster[37]
SiO_2 gel B	i-C_3H_7OH	5.0	5.6	7.0	Foster[37]
SiO_2 gel B	n-C_4H_9OH	5.3	6.0	7.8	Foster[37]
SiO_2 gel	H_2O	3.1	3.5	6.1	Anderson[5]
SiO_2 gel 7	C_2H_5OH	4.6	5.2	6.1	Anderson[5]
SiO_2 gel 7	C_6H_6	5.3	5.9	6.8	Anderson[5]
SiO_2 gel 6	C_2H_5OH	4.6	5.2	8.0	Anderson[5]
SiO_2 gel	H_2O	3.1	3.5	4.8	Van Bemmeln[38]
Fe_2O_3 gel	CH_3OH	4.1	4.6	8.1	Foster[39]
Fe_2O_3 gel	n-C_3H_7OH	5.0	5.6	8.9	Foster[39]
Fe_2O_3 gel	n-C_4H_9OH	5.3	6.0	8.6	Foster[39]
Fe_2O_3 gel	C_6H_6 (40°)	5.3	6.0	6.1	Lambert and Clark[40]
Fe_2O_3 gel	C_6H_6 (50°)	5.3	6.0	6.2	
Fe_2O_3 gel	C_6H_6 (60°)	5.4	6.1	7.6	
Fe_2O_3 gel	C_6H_6 (40–60°)	5.3	6.0	6.5	Foster[14]
Fe_2O_3 gel	C_2H_5OH (60–70°)	4.7	5.3	7.5	Foster[14]
Fe_2O_3 gel A	C_2H_5OH (60°)	4.7	5.2	7.0	Lambert and Foster[41]
Fe_2O_3 gel A	C_6H_6 (60°)	5.4	6.1	7.6	
Fe_2O_3 gel A	C_6H_6 (50°)	5.3	6.0	7.5	
Fe_2O_3 gel A	C_6H_6 (40°)	5.3	6.0	6.8	
Fe_2O_3 gel B	C_2H_5OH (60°)	4.7	5.3	16.1	
Fe_2O_3 gel B	C_6H_6 (60°)	5.4	6.1	16.3	
Fe_2O_3 gel B	C_6H_6 (50°)	5.3	6.0	17.0	
Fe_2O_3 gel B	C_6H_6 (40°)	5.3	6.0	14.6	
Charcoal A[42]	H_2O	3.1	3.5	4.2	Burrage[43]
Charcoal, birchwood air activated	CH_3OH	4.1	4.6	2.5	Burrage[44]
Charcoal, birchwood air activated	CCl_4	5.4	6.1	4.0	Burrage[44]

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(35) The initial adsorption curve illustrates an unlimited and irreversible type of hysteresis possibly due to imperfect rigidity in the gel structure. This latter type of hysteresis is a different phenomena from that under discussion here.

(36) A. G. Foster, *Proc. Roy. Soc.* (London), **A146**, 129–140 (1934).

(37) *Ibid.*, **A150**, 77–83 (1935).

(38) Van Bemmeln, *Z. anorg. allgem. Chem.*, **13**, 233–356 (1897).

(39) A. G. Foster, *Proc. Roy. Soc.* (London), **A147**, 128–140 (1934).

(40) B. Lambert and A. M. Clark, *ibid.*, **A122**, 497–512 (1929).

(41) B. Lambert and A. G. Foster, *ibid.*, **A136**, 363–377 (1932).

(42) P. G. T. Hand and D. O. Shiels, *J. Phys. Chem.*, **32**, 441–455 (1928).

(43) L. J. Burrage, *Trans. Faraday Soc.*, **29**, 665–678 (1933). These and the following results on charcoal are presented with reservations as the adsorption mechanism on charcoal may be due to monolayer adsorption and the hysteresis caused by lack of rigidity or interference of foreign materials such as carbon oxides.

(44) *Ibid.*, **30**, 317–325 (1934).

TABLE I (*Concluded*)

Sorbent	Sorbate	D_{cubic}, Å.	$D_{\text{spherical}}$, Å.	D, Å., calcd. from Eq. 6	Investigator
Charcoal, birchwood air activated	CS_2	4.6	5.2	4.0	Burrage[44]
Charcoal Nl	CH_3OH	4.1	4.6	2.5	Burrage[44]
Charcoal, $ZnCl_2$ activated	C_2H_5OH	4.6	5.2	3.0	Burrage[44]
Charcoal, almond shell[45]	C_3H_7OH	5.0	5.6	4.0	Burrage[44]
Charcoal, almond shell	HCOOH	4.0	4.5	4.0	Burrage[44]
Charcoal	H_2O	3.1	3.5	4.5	Gustaver[19]
TiO_2 gel	H_2O	3.1	3.5	6.8	Rao[17]
TiO_2 gel	H_2O	3.1	3.5	5.4	Rao[17]
SiO_2 gel	H_2O	3.1	3.5	4.6	Rao[17]
SiO_2 gel	CCl_4	5.4	6.1	5.8	Rao[17]
Fe_2O_3 gel	H_2O	3.1	3.5	6.8	Rao[17]
Fe_2O_3 gel	CCl_4	5.4	6.1	6.4	Rao[17]
SiO_2 gel	H_2O	3.1	3.5	3.9	Pidgeon[46]
SiO_2 gel (heated at 300°)	H_2O	3.1	3.5	3.9	Pidgeon[46]

In judging the agreement obtained in Table I between D calculated from equation (6) and D_{cubic} or $D_{\text{spherical}}$ calculated from the density of the liquid sorbate the following points must be considered:

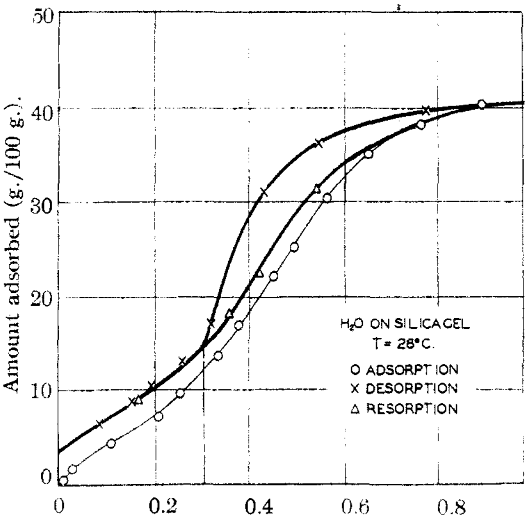

Fig. 2.

1. In order to apply the open pore theory to the determination of the point of hysteresis inception, open (or constricted) pores of radius just larger than 2D must be present in the sorbent. If pores in this region are absent, hysteresis cannot begin until pressures are reached corresponding to the open pores which are present. In such a case, the value of $D(= r_c/2)$ calculated from equation (6) would be larger than either D_{cubic} or $D_{\text{spherical}}$ and would be a measure not of the thickness of the adsorbed layer but of the radius, r_c, of the smallest open pores present. This may be the case for some of the Fe_3O_3 gels and particularly for Lambert and Foster's[40] Fe_2O_3 gel B which was prepared by heating gel A several hours at 148° in the presence of water vapor. On the other hand, the behavior of Higuti's TiO_2 gel with many different sorbates indicates that for this sorbent sufficiently small pores are present.

2. The capillary theory according to which adsorption consists of monolayer formation followed by capillary condensation is, as stated in the introduction, only a first approximation. Depending on the conditions—specific nature of the sorbent and sorbate, temperature, etc.—more or less than a monolayer could conceivably form prior to capillary condensation. For example, suppose that conditions are such that the multilayer adsorption mechanism yields a value P_3 for the equilibrium pressure for the essential completion of the third adsorbed molecular layer. Now if P_3 is less than P_d calculated from equation (3) with $r_c = 3D$ then generally speaking condensation will occur at P_3 instead of P_a, evaporation will also occur at P_3 instead of P_d and no hysteresis will be present at this pressure. In such cases, if one should try to calculate P_h from equation (5) the result would be lower than the observed value for P_h. Conversely if the observed value for P_h were used in equation (6) to calculate D, a higher value than the molecular diameter would be obtained. This is another possible explanation of the behavior of some of the Fe_2O_3 gels.

3. Equation (6) assumes that wetting is complete ($\theta = 0$) and that true equilibrium is attained. Any impurity, such as permanent gases in the apparatus, which would prevent the realization of these conditions would exclude the system as a suitable one for testing the theory. For this reason, isotherms determined in the presence of permanent gases are not included in Table I. As pointed out previously, such isotherms usually show an unlimited hysteresis which is not completely reversible. The low results for charcoal may be due to the presence of gases which could not be removed by ordinary evacuation.

4. For sorbents which cannot be considered

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(45) *Ibid.*, **29**, 564–576 (1933).

(46) L. M. Pidgeon, *Can. J. Research*, **10**, 713–729 (1934).

rigid, both the surface area and pore volume are different on adsorption than on desorption and hysteresis cannot be explained on the open pore theory alone. Hysteresis in such a system is likely to be unlimited and will be further complicated by drift if the swelling is not entirely reversible. Because of these difficulties systems which swell markedly such as wood and cotton cellulose have not been included.

5. Finally, exact agreement between D and D_{cubic} or $D_{\text{spherical}}$ should not be expected for unsymmetrical molecules. For molecules oriented perpendicularly to the surface, D should be greater than D_{cubic} or $D_{\text{spherical}}$. Examination of the table shows that molecules such as CH_3OH which might be expected to orient perpendicular to an oxide surface do have higher values for D than indicated by D_{cubic} or $D_{\text{spherical}}$.[47]

Examination of Table I reveals that except for the few cases pointed out in the preceding discussion, equation (6) is in good agreement with the experimental results and in particularly good agreement with Higuti's series of measurements on TiO_2 gel.

Additional support for equation (6) is found in the effect of temperature on the point of hysteresis inception. As long as temperature changes are not so great that the way in which the molecule is attached to the surface is altered, D should not vary with the temperature to a greater extent than does the density. Higuti has determined P_h for most of the systems reported in Table II from 0 to 30°. Although P_h/P_0 varies in this range by 25% or more for some of the sorbates, D, in most cases, varies by less than 5%, which may be considered within experimental error.

Scanning the Hysteresis Loop

"Scanning" the hysteresis loop is the name given by Rao[17] to the experimental process in which desorption is begun from an adsorption equilibrium point below saturation such as point (1), Fig. 3. The system follows the path labeled "b" in Fig. 3 and meets the desorption branch of the isotherm at some point (2) above the point of hysteresis inception.[48]

Considering a sorbent system consisting of a continuous range of open cylindrical pores and also a range of conical pores, the equilibrium pressure, P_a/P_0, at the point (1) will correspond to a capillary radius, r_c given by equation (2).

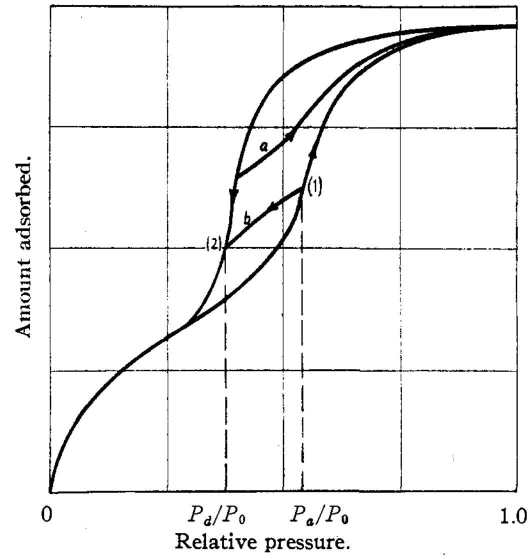

Fig. 3.

In this case, r_c is the radius of the largest open capillary to have filled at point (1). As the pressure is reduced, desorption occurs at once from the conical pores but not from the open pore of radius r_c until the pressure, P_d/P_0, given by equation (3) is reached.[49] At this point, the system will be in the same condition in which it would have been had desorption occurred from saturation. In other words, P_d/P_0 is the pressure at point (2) where curve "b" meets the desorption branch of the isotherm. From equations (2) and (3) the relation between P_d/P_0 and P_a/P_0 is[50]

$$P_d/P_0 = (P_a/P_0)^{2(r_c-D)r_c} \tag{7}$$

In Table II values for P_d/P_0 calculated from equation (7) are compared with available experi-

TABLE II

Sorbent	Sorbate	$(P_a/P_0)_{\text{exp.}}$	$(P_d/P_0)_{\text{exp.}}$	$(P_d/P_0)_{\text{calcd.}}$	Investigator
TiO_2 gel	H_2O	0.88	0.78	0.79	Rao[17]
TiO_2 gel	H_2O	.86	.75	.76	Rao[17]
TiO_2 gel	H_2O	.82	.73	.71	Rao[17]
TiO_2 gel	H_2O	.79	.71	.67	Rao[17]
SiO_2 gel	H_2O	.60	.38	.49	Rao[17]
SiO_2 gel	H_2O	.53	.36	.44	Rao[17]
SiO_2 gel	H_2O	.47	.35	.40	Rao[17]
SiO_2 gel	CCl_4	.32	.25	.26	Rao[17]
Fe_2O_3 gel	CCl_4	.57	.43	.43	Rao[17]
Fe_2O_3 gel	CCl_4	.49	.40	.37	Rao[17]
SiO_2 gel	H_2O	.55	.42	.44	Van Bemmeln[38]
SiO_2 gel	H_2O	.53	.39	.43	Van Bemmeln[38]

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[47] It is worth noting that higher alcohols such as C_2H_5OH and C_3H_7OH have values for D closer to D spherical than does CH_3OH. Possibly chain bending may result in the former molecules occupying a less unsymmetrical volume element. It so happens as will be shown in another paper that the values for the area of Higuti's TiO_2 gel calculated from the data for the 18 different sorbates in Table I are remarkably consistent if one uses the asymmetry factor indicated by the value of D for the different sorbates. Consistency is not nearly so good if the sorbates are assumed symmetrical.

[48] On adsorbing from a desorption equilibrium point, a similar scanning curve, "a" in Fig. 3, is obtained. Rao found that for the sorbents he used scanning curves of this type did not rejoin the adsorption curve until saturation was reached.

[49] Sorbate held reversibly in mono or polylayers would also begin to desorb as soon as the pressure is reduced. For an adsorption equation including both polylayer adsorption and capillary condensation see A. A. Schuchowitzki, *Kolloid-Z.*, **66**, 139–147 (1934). A small amount of sorbate would also be lost from open capillaries due to a change in curvature of the meniscus.

[50] In a previous paper[30] the relation $P_a^2 = P_0P_d$ was given for D negligible compared to r_c. In this case equation (7) reduces to the simple form.

mental data. Equation (2) was used to calculate r_c; D_{H_2O} and D_{CCl_4} were taken as 4.4 and 6.3 Å., respectively.

The structure of the sorbent will be an important factor in determining the accuracy with which P_d/P_0 is predicted by equation (7). For example, $(P_d/P_0)_{calcd.}$ will be less than $(P_d/P_0)_{exp.}$ if:

1. The pores causing hysteresis are bottle shaped with $r_b/r_n < 2(r_c - D)/r_c$ where r_b is the radius of the body of the pore and r_n is the radius of the neck. In this case

$$P_a/P_0 = e^{-2\sigma V/r_bRT}$$

$$P_d/P_0 = e^{-2\sigma V/r_nRT}$$

$$P_d/P_0 = (P_a/P_0)^{r_b/r_n} \qquad (8)$$

and the joining of the scanning curve and desorption isotherm would occur at P_d/P_0, given by equation (8) which is higher than the value—$(P_d/P_0)_{calcd.}$—obtained from equation (7) if $r_b/r_n < 2(r_c - D)/r_c$.

2. Flat sided clefts are present for which

$$W < r_v < 2(W - D) \text{ or approximately } W < r_v < 2W \qquad (9)$$

where W is the distance between walls in the flat sided cleft and r_v is the largest radius in the cavity below the cleft, the cavity being assumed to have a circular cross section. For the flat sided cleft portion of the pore shown in Fig. 4

$$P_a/P_0 = e^{-2\sigma V/r_vRT} \qquad (10)$$

$$P_d/P_0 = e^{-\sigma V/(W/2)RT} \qquad (11)$$

whence

$$P_d/P_0 = (P_a/P_0)^{r_v/W} \qquad (12)$$

Thus P_d/P_0 will be greater than $(P_d/P_0)_{calcd.}$ obtained from equation (7) when $r_v/W < 2(r_c - D)/r_c$. Comparing equations (2) and (10) an open cylindrical pore which will have the same P_a/P_0 as the cleft of Fig. 4 must have $r_c - D = r_v/2$. Substituting for r_c in terms of r_v the cleft will have a higher P_d/P_0 than $(P_d/P_0)_{calcd.}$ when

$$r_v/W < r_v/(r_v/2 + D) \qquad (13)$$

or

$$r_v < 2(W - D) \qquad (14)$$

from which equation (9) follows since for $r_v \gtreqless W$ the cleft does not contribute to hysteresis.

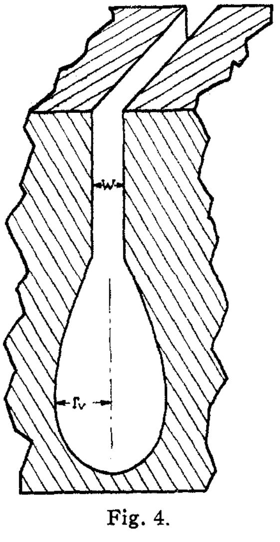

Fig. 4.

In the above instances almost all the pores present must be of type (1) or (2) since even a small fraction of open cylindrical pores would prevent the scanning curve from actually joining the desorption branch until $(P_d/P_0)_{calcd.}$ is reached. A glance at Table II shows that in the few cases in which $(P_d/P_0)_{calcd.}$ differs from $(P_d/P_0)_{exp.}$ by more than experimental error, $(P_d/P_0)_{calcd.}$ is greater, not less than $(P_d/P_0)_{exp.}$[51]

On the other hand $(P_d/P_0)_{calcd.}$ will be greater than $(P_d/P_0)_{exp.}$ if:

3. Bottle shaped pores having $r_b/r_n > 2(r_c - D)/r_c$ are present.

4. Clefts are present for which

$$r_v > 2(W - D) \text{ or approximately } r_v > 2W \qquad (15)$$

where W and r_v have their previous meaning. Equation (15) can be derived in the same manner as equation (9) by replacing the less than signs by greater than signs.

For pores of type (3) and (4), P_d/P_0 as given by equations (8) and (12), respectively, is lower than $(P_d/P_0)_{calcd.}$ from equation (7). Thus the scanning curve will join the desorption branch below the point corresponding to $(P_d/P_0)_{calcd.}$. Moreover the presence of only a small fraction of either of these pore types even in a system of predominantly open or constricted pores will prevent joining at $(P_d/P_0)_{calcd.}$ thus causing $(P_d/P_0)_{exp.}$ to be less than $(P_d/P_0)_{calcd.}$.[52]

In assuming that bottle shaped pores of type (1) and (3) above affect the scanning curves it is assumed that the bottle neck theory of hysteresis is valid, *i. e.*, that during desorption the liquid column in a bottle shaped pore remains intact and equilibrium is not reached. This may be open to argument; however, the effect of clefts on the scanning curve is, of course, quite independent of the validity of the bottle neck theory.

The results in Table II provide a fairly good check on equation (7). The tendency for $(P_d/P_0)_{calcd.}$ to be larger than the experimental value for Rao's SiO_2 gel may indicate presence of some clefts of type (4) even down to fairly small pore sizes. Additional data with other systems would be desirable. The preceding discussion also indicates how scanning curves may be used to throw light on the structure of the pores of a sorbent.

The evidence presented in support of equations (6) and (7) implies that: (1) The capillary theory is a satisfactory first approximation for most of the systems considered. (2) Both σ and V are about the same in capillaries as fine

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(51) The experimental values in Table II had to be taken from published curves as tables of data were not available. The accuracy of determining P_a and P_d is probably not much better than several per cent. of the saturation pressure.

(52) Clefts for which $r_v > > W/2$ are not likely to affect type "b" curves (Fig. 3) because r_v is so large that adsorption cannot occur until close to saturation. However, such structures would markedly influence type "a" curves (Fig. 3) since they would remain filled until fairly low pressures and would prevent the coincidence of the "a" curves with the adsorption branch until close to saturation. The behavior of Rao's type "a" curves can be explained in this way. A. J. Allmand, P. G. T. Hand and J. E. Manning, *J. Phys. Chem.*, **33**, 1694–1712 (1929), pp. 1706–1708, report type "a" scanning curves for charcoal which rejoin the adsorption isotherm at pressures below the upper end of the hysteresis loop. Unfortunately, no data are given from which calculations can be made. It appears plausible that clefts and large cavities are more likely to be present in oxide gels such as used by Rao than in charcoal.

as $r_c = 2D$ as they are in bulk. (3) The open pore theory appears to be in most cases a satisfactory explanation of hysteresis. However, departure of experimental values from predicted values in a few instances indicates that the presence of other factors must also be considered.

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Summary

1. Several predictions based on the capillary theory of adsorption and the open pore theory of hysteresis have been shown to agree reasonably well with experimental data.

2. The agreement between theory and experiments indicates that the capillary theory of adsorption which postulates the formation of a monomolecular layer followed by capillary condensation is a fairly good first approximation for the adsorption mechanism in the systems considered.

3. The surface tension and molal volume of a liquid confined in a capillary of radius only twice the diameter of the liquid molecule appear to be about the same as for the liquid in bulk.

CHICAGO, ILLINOIS RECEIVED OCTOBER 21, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Molecular Surface Energy of Sulfur Dioxide Addition Compounds. III[1]

BY JOSEPH J. JASPER AND J. RUSSELL BRIGHT[2]

The effect of temperature on the molecular surface energy of several liquid addition compounds of tertiary aliphatic amines with sulfur dioxide has been described in earlier articles.[3]

A more complete interpretation of the temperature effects described necessarily involves the extension of this series of studies to tertiary amine-sulfur dioxide addition compounds of still greater molecular weight. The purpose of this investigation, therefore, was to determine, for comparison with those preceding, the same physico-chemical constants for the respective equi-molecular mixtures of tripropylamine and tributylamine with sulfur dioxide.

Preparation of the Liquid Molecular Addition Compounds

The methods for purifying the materials were similar to those previously described.[3] Pure anhydrous sulfur dioxide was bubbled slowly through a known quantity of the best grade of Eastman Kodak Company tripropylamine (n^{25}D 1.4151) until equi-molar quantities of the reactants were present. Since considerable heat was evolved during the reaction, the temperature was maintained at about 18° to prevent decomposition of the product. Upon further cooling, the product crystallized into light yellow needles, which melted at 15.3°. Distillation, even under reduced pressure, was impossible. The freshly prepared addition compound (n^{25}D 1.4740) was analyzed for nitrogen by a modified Kjeldahl method; calculated for $(C_3H_7)_3N$:SO_2, N, 6.76. Found: N, 6.35, 6.46.

This compound is stable for an indefinite period as a light yellow solid at ice-box temperatures. It is very hygroscopic, changing to a red-brown liquid upon exposure to moist air. At temperatures above 45°, it changed to a black liquid whose density and surface tension deviated considerably from the linear relations given in a following paragraph.

Cryoscopic determination of the molecular weight, using purified benzene (f. p. 5.4°) as the solvent, gave 207.7, 208.4, 207.6 in 0.0327 weight molal solutions; theoretical 207.27. Increasing concentrations gave the molecular weights; 0.163 M, 2115.5; 0.327 M, 318.3; 0.411 M, 322.5. Similar association was observed by Bright and Fernelius[4] with the addition compound dimethylaniline-sulfur dioxide in the solvent dimethylaniline. Since the addition products are very hygroscopic, special precautions were used in their transfer to the various apparatus employed. Density and surface tension measurements were made, using the same apparatus and technique previously described.[3b] The viscosimeter used was constructed according to the design and specifications of Jones and Fornwalt.[5]

Experimental data are presented in Tables I and II. From these it is evident that the density d and surface tension γ are linear functions of the temperature for the compound tripropylamine-sulfur dioxide over the range 18 to 45°. These relations are given by the following equations

$$d = 1.0174 - 1.069 \times 10^{-3}t$$
$$\gamma = 32.72 - 0.125t$$

The average deviation of the data from the d-curve and γ-curve is, respectively, 0.02 and 0.08%. The Eötvös constant is −3.77 and, therefore, is less than the average value of −2.12, which is commonly assigned to non-polar liquids. This would seem to indicate considerable association, according to the criteria of Walden and Swinne.[6]

An observed value of 488.7 for the parachor of the $(C_3H_7)_3N:SO_2$ compound is in good agreement with the value of 503 obtained from the sum of

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(1) Abstracted in part from material presented before the Symposium on Molecular Addition Compounds of the Division of Physical and Inorganic Chemistry at the Pittsburgh meeting of the American Chemical Society, September 6, 1943.

(2) Present address: Gelatin Products Co., Detroit, Michigan.

(3) Bright and Jasper, THIS JOURNAL, (a) **63**, 3486 (1941); (b) **65**, 1262 (1943).

(4) Bright and Fernelius, THIS JOURNAL, **65**, 637 (1943).

(5) Jones and Fornwalt, *ibid.*, **60**, 1683 (1938).

(6) Walden and Swinne, *Z. physik. Chem.*, **82**, 271 (1913).