

produced by impurities in the salts is not involved in this effect. Samples of potassium nitrate obtained from three very different sources gave identical salt effects. Two samples of sodium sulfate, one impure, the other highly purified, gave results identical within the limit of experimental error.

The salt effect is caused by a depression of the double-layer zeta-potential of the silver bromide.⁵ This permits a greater penetration of the bivalent ascorbic acid ions through the double-layer region to the surface of the grain, where the development reaction takes place.

Summary

The course of photographic development by

l-ascorbic and *d*-iso-ascorbic acids is not affected by the oxidation products. The iso-ascorbic acid reacts at a somewhat greater rate than the ascorbic acid.

At pH 10 or above, the active developer consists almost entirely of the bivalent ion. This ion is adsorbed prior to reaction with the silver bromide. In caustic solution, diffusion rates become important in determining the measured development rate.

The rate of development is markedly dependent upon the nature and concentration of the salts present. The rate increases with increasing salt concentration.

ROCHESTER, N. Y.

RECEIVED OCTOBER 4, 1943

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Molecular Structures of Dimethyl Silicon Dichloride, Methyl Silicon Trichloride and Trifluoro Silicon Chloride¹

BY R. L. LIVINGSTON AND L. O. BROCKWAY

Previous study of the mutual interaction of groups attached to a central silicon atom left several unanswered questions. For example, the substitution of one or two hydrogen atoms into silicon tetrachloride has no detectable effect on the length of the Si-Cl bond,² but in silicon tetramethyl the replacement of one methyl group by a silicon atom (as in the molecule $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$)³ apparently shortens the Si-C bonds by one and one-half per cent. An extension of the study of the interaction between atoms attached to silicon was made possible by the availability of samples of methyl silicon trichloride and dimethyl silicon dichloride. Another question of interest in silicon compounds is the interaction of attached fluorine atoms. In the organic fluorides the presence of two or more fluorine atoms on the same carbon shortens the C-F bond by 0.06 Å. below the length observed in the monofluorides,⁴ while the effect of the CF_3 group in CF_3Cl ⁵ on the attachment of the chlorine atom is equally marked in comparison with the bond lengths in carbon tetrachloride. This effect in the analogous silicon compound has now been studied. The methyl silicon chlorides were supplied by W. F. Gilliam of the General Electric Research Laboratories, and the trifluoro silicon chloride was supplied by H. S. Booth of Western Reserve University.

(1) This paper represents part of a dissertation submitted to the Horace H. Rackham School of Graduate Studies by R. L. Livingston in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(3) L. O. Brockway and N. R. Davidson, *THIS JOURNAL*, **63**, 3287 (1941).

(4) L. O. Brockway, *J. Phys. Chem.*, **41**, 747 (1937).

(5) L. O. Brockway and John H. Sechrist, in publication.

Electron diffraction photographs of the vapors were prepared in the usual way using an electron wave length of 0.0592 Å. and a camera distance of 10.29 cm. The specimens were handled on a vacuum line and transferred to the camera without admitting air in order to reduce possible hydrolysis by water vapor. For each compound the s_0 values $(4\pi(\sin \theta/2)/\lambda)$ calculated from the visually measured ring diameters are tabulated together with the coefficients used in the radial distribution function, $D(r) = \sum C_k \sin s_k r / s_k r$. The radial distribution curves (Fig. 1) indicate by their stronger maxima the values of interatomic distances associated with the more important scattering terms.

Methyl Silicon Trichloride.—Photographs of methyl silicon trichloride taken with the sample held near 25° show nine rings in the range out to $s = 23$. The measurements on the last eight are listed in Table I. The fourth maximum appears as a satellite to the stronger third maximum; its measured position is accordingly unreliable. The sixth maximum is broad with a faint inner shelf which was not measured. The eighth minimum is broad without a well-defined lightest point.

Scattering curves were calculated for four models in each of which the Si-C bond was assumed to lie on an axis of trigonal symmetry, the methyl group was assumed to have the regular tetrahedral bond angles with C-H = 1.09 Å., and the Si-Cl distance was set at 2.00 Å. to fix the scale of the models. In three models the Si-C/Si-Cl ratio was 0.970 with the $\angle \text{ClSiCl}$ equal to 113° (model A), to 109½° (model B) and to 106° (model D). In model C the bond distance ratio was 0.935 with a chlorine bond

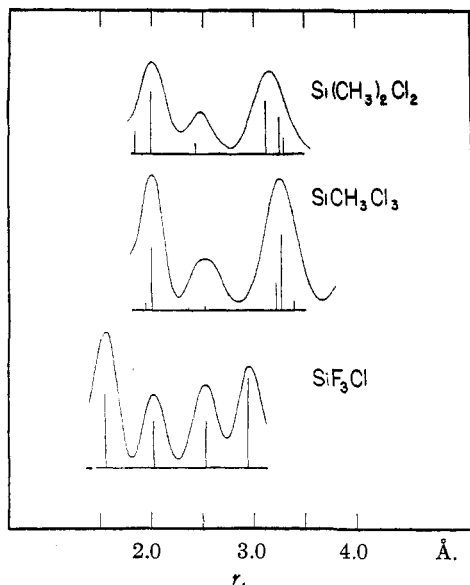


Fig. 1.—Radial distribution curves. The vertical lines show the relative scattering power associated with the interatomic distances in the final models.

angle of $109\frac{1}{2}^\circ$. The coefficients of the Si-C and C-Cl terms were so small relative to those for the SiCl and Cl-Cl terms that the change from model B to C is scarcely detectable in the curves (Fig. 2). This means that the scattering power of the carbon atoms is so small in comparison with the silicon and three chlorine atoms that its position cannot be fixed by the diffraction data.

Curves B and C reproduce the characteristic features of the photographs: the weaker fourth ring, the sixth with the inner shelf, and the in-

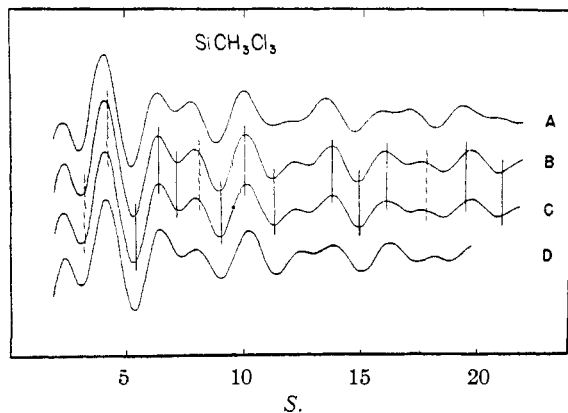


Fig. 2.—Theoretical electron scattering curves for SiCH_3Cl_3 . The positions of the maxima and minima observed on the photographs are indicated.

definite eighth minimum observed in the photographs falling on a very weak peak in both of the curves. The $3\frac{1}{2}^\circ$ change in bond angle either up or down leads to curves which are somewhat less satisfactory. Curve A (113°) shows the fourth peak too strong, no inner shelf on the sixth and the seventh is followed by an equally prominent ring which does not appear on the photographs, curve D shows faults of the opposite sense at the same positions although its deviations from B are not as marked as those of A. Accordingly, we choose for the Cl-Si-Cl angle the value $109 \pm 3^\circ$. The comparison of observed and calculated s values (Table I) leads to the value $3.27 \pm 0.03 \text{ \AA.}$ for the Cl-Cl distance and to $2.01 \pm 0.02 \text{ \AA.}$ for the Si-Cl distance. No definite value is given for the Si-C distance since the uncertainty in its direct determination would be greater than 0.1 \AA. The values reported here are shown by vertical lines in the radial distribution figure together with a line marking the position of C-Cl if Si-C were 1.9 \AA.

Dimethyl Silicon Dichloride.—The dimethyl silicon dichloride was photographed at temperatures from 0 to 40° . Fifteen maxima and minima were measured out to $s = 19.3$ as listed in Table II. The less reliable s_0 values are enclosed in parentheses and shown on the curves (Fig. 3) by dotted lines. The radial distribution curve (Fig. 1) shows strong peaks at 1.98 \AA. and 3.16 \AA. The first is due to the bonded pairs, Si-Cl and Si-C, while the second is due mainly to C-Cl and Cl-Cl.

Scattering curves were calculated for the seven models in Table III, the Si-Cl distance being fixed at 2.00 \AA. and the methyl group with the regular $109\frac{1}{2}^\circ$ bond angle and C-H = 1.09 \AA. in each. Of the five curves with $109\frac{1}{2}^\circ$ angles on the Si atom only D and E show the right qualitative features. The fourth maximum is too strong in B and C and too weak in F; the inner shelf on the sixth is too small in B and C and does not appear at all in F. Model A

TABLE I

METHYL SILICON TRICHLORIDE

| Max. | Min. | s_0 | C_k | S_B/S_0 | S_C/S_0 |
|------|------|----------------------|-------|-----------|-----------|
| | 2 | 3.33 | - 1 | (0.940) | (0.946) |
| 2 | | 4.30 | 17 | (.972) | (.986) |
| | 3 | 5.43 | -13 | .985 | .981 |
| 3 | | 6.44 | 17 | 1.002 | 1.002 |
| | 4 | 7.19 | -12 | 1.013 | 1.017 |
| 4 | | (8.14) | 15 | (0.977) | (0.983) |
| | 5 | 9.07 | -34 | 0.994 | 1.011 |
| 5 | | 10.07 | 25 | 1.005 | 1.012 |
| | 6 | 11.22 | - 7 | 1.005 | 1.009 |
| 6 | | 13.66 | 16 | 1.007 | 1.012 |
| | 7 | 14.83 | -24 | 1.005 | 1.006 |
| 7 | | 16.07 | 8 | 1.000 | 1.002 |
| | 8 | (17.76) | - 7 | | |
| 8 | | 19.45 | 7 | 1.015 | 1.014 |
| | 9 | 21.00 | - 6 | 0.994 | 0.995 |
| 9 | | (22.45) | 5 | | |
| | | Average | 1.002 | 1.006 | |
| | | Average deviation | 0.007 | 0.008 | |
| | | Cl-Cl, \AA. | 3.27 | 3.28 | |
| | | Si-Cl, \AA. | 2.00 | 2.01 | |

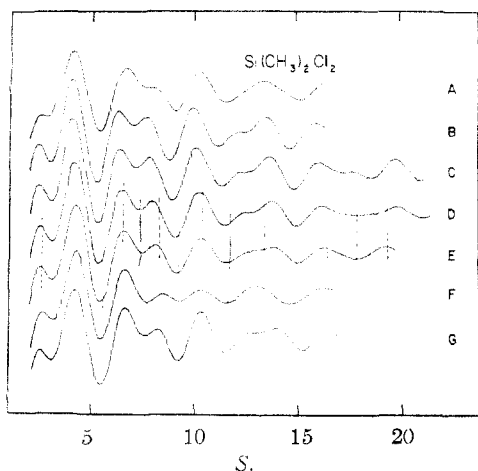


Fig. 3.—Theoretical scattering curves for $\text{Si}(\text{CH}_3)_2\text{Cl}_2$.

with a Cl-Si-Cl angle of 113° is also not good while Model G ($\angle\text{Cl-Si-Cl} = 106^\circ$) shows fair qualitative agreement. No systematic variation of the C-Si-C angle was attempted because of the small contributions of the Si-C and C-C terms. The quantitative comparison of observed and calculated s values given in Table II makes model G unsatisfactory because of the large average deviations from the mean value of the s/s_0 ratios. Definite values are reported for the three strongest terms on the basis of

| Max. Min. | s_0 | C_k | S_D/S_0 | S_E/S_0 | S_G/S_0 |
|-------------------|---------|-------|-----------|-----------|-----------|
| 1 | (2.56) | 6 | (0.977) | | |
| 2 | (3.37) | - 5 | (.926) | | |
| 3 | (4.40) | 17 | (.950) | | |
| 4 | 5.58 | -17 | .970 | 0.975 | 0.984 |
| 5 | 6.53 | 19 | 1.003 | 1.008 | 1.025 |
| 6 | 7.37 | - 7 | 0.996 | 1.019 | 1.042 |
| 7 | (8.29) | 13 | (.962) | | |
| 8 | 9.25 | -14 | .984 | 0.995 | 0.997 |
| 9 | 10.40 | 20 | .991 | 1.001 | .999 |
| 10 | 11.73 | -20 | .981 | 0.991 | .983 |
| 11 | (13.40) | 15 | (1.036) | | |
| 12 | 14.95 | - 9 | 1.008 | 1.013 | 1.023 |
| 13 | 16.43 | 4 | 0.992 | 0.992 | 1.002 |
| 14 | (17.87) | - 3 | | | |
| 15 | (19.34) | | | | |
| Average | | | 0.991 | 0.999 | 1.007 |
| Average deviation | | | 0.009 | 0.011 | 0.017 |

| | Si-C | $\angle\text{Cl-Si-Cl}$ | $\angle\text{C-Si-C}$ |
|---|--------|-------------------------|------------------------|
| A | 1.87 Å | 113° | $105\frac{1}{2}^\circ$ |
| B | 2.04 | $109\frac{1}{2}$ | $109\frac{1}{2}$ |
| C | 1.94 | $109\frac{1}{2}$ | $109\frac{1}{2}$ |
| D | 1.87 | $109\frac{1}{2}$ | $109\frac{1}{2}$ |
| E | 1.80 | $109\frac{1}{2}$ | $109\frac{1}{2}$ |
| F | 1.67 | $109\frac{1}{2}$ | $109\frac{1}{2}$ |
| G | 1.87 | 106 | $112\frac{1}{2}$ |

models D and E; Si-Cl = 1.99 ± 0.03 Å.; Cl-Cl = 3.25 ± 0.04 Å. and C-Cl = 3.12 ± 0.06 Å.

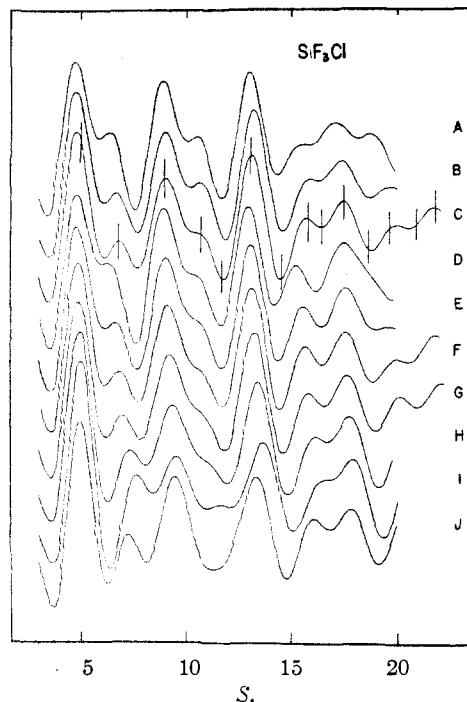


Fig. 4.—Theoretical scattering curves for SiF_2Cl .

The carbon atom positions are somewhat indefinite, although the relative importance of the carbon atom scattering is more favorable than in the trichloride. The carbon-chlorine term is nearly equal to the silicon-chlorine term, and the C-Cl distance reported above is reliable within the range given. The Si-C distance, however, can be calculated only if one of the bond angles involving carbon can be fixed. It may be supposed that since the Cl-Si-Cl angle has the regular tetrahedral value within 2 or 3° the bond angle between the two Si-C bonds will also not differ much from the regular value. With the assumption of $109\frac{1}{2}^\circ$ for the angle C-Si-C, the Si-C distance becomes 1.83 Å. with an estimated uncertainty of ± 0.06 Å., allowing some for a deviation of the angle from the assumed value.

Trifluoro Silicon Chloride.—Nine distinct rings appear in the photographs of trifluorosilicon chloride taken with the sample at temperatures from -115 to -85° . The distinctive features of the pattern are a faint shelf on the outer edge of the third and a very faint second maximum followed by successively stronger third and fourth peaks. The measured s_0 values are given in Table IV.

The radial distribution curve (Fig. 1) has two strong peaks at 1.55 and 2.95 Å. and two weak ones at 2.02 and 2.53 Å. These may be immediately recognized as associated with the distances Si-F, Cl-F, Si-Cl and F-F in the order

given. The weaker terms are probably less reliable since they lack about 1% of being compatible with the stronger terms.

TABLE IV
TRIFLUOROSILICON CHLORIDE

| Max. | Min. | S_0 | C_k | S_e/S_0 | S_f/S_0 | S_g/S_0 |
|-------------------|------|-------|-------|-----------|-----------|-----------|
| 1 | | 5.06 | 45 | 0.958 | 0.961 | 0.966 |
| 2 | | 6.86 | 8 | 1.001 | .999 | 1.020 |
| 3 | | 9.03 | 44 | 1.007 | 1.010 | 1.023 |
| 4 | | 10.78 | 7 | | | |
| | 5 | 11.79 | -77 | 1.005 | 0.995 | 1.003 |
| 5 | | 13.12 | 75 | 1.007 | 1.002 | 1.013 |
| | 6 | 14.61 | -68 | 0.996 | 0.995 | 1.004 |
| 6 | | 15.88 | 30 | .996 | 0.998 | 1.000 |
| | 7 | 16.51 | -15 | .999 | 1.000 | 1.007 |
| 7 | | 17.56 | 28 | .998 | 1.001 | 1.007 |
| | 8 | 18.70 | -26 | 1.007 | 1.009 | 1.014 |
| 8 | | 19.69 | 12 | 1.016 | 1.016 | 1.023 |
| | 9 | 20.92 | -5 | 0.984 | 0.981 | 1.002 |
| 9 | | 21.80 | 5 | .996 | .998 | 1.012 |
| Average | | | | .998 | .997 | 1.007 |
| Average deviation | | | | .009 | .009 | .009 |

TABLE V
MODELS FOR TRIFLUOROSILICON CHLORIDE

| Model | \angle F-Si-Cl | Si-Cl/Si-F |
|-------|-------------------|------------|
| A | 112° | 1.350 |
| B | 112° | 1.312 |
| C | 110 $\frac{1}{2}$ | 1.312 |
| D | 109 $\frac{1}{2}$ | 1.390 |
| E | 109 $\frac{1}{2}$ | 1.350 |
| F | 109 $\frac{1}{2}$ | 1.329 |
| G | 109 $\frac{1}{2}$ | 1.312 |
| H | 109 $\frac{1}{2}$ | 1.270 |
| I | 109 $\frac{1}{2}$ | 1.230 |
| J | 106 | 1.312 |

Ten models were calculated having a trigonal axis through the Si-Cl bond and the bond angles and bond distances given in Table V. The Si-F distance was set at 1.54 Å. except in models C and F where it was 1.55 Å. None of the curves D to I (109 $\frac{1}{2}$ ° models) is entirely satisfactory. In D the weak second maximum is not sufficiently resolved from the first and the shelf on the third is too weak. The other 109 $\frac{1}{2}$ ° models in order get better in the first respect but worse in the second while the fifth and sixth peaks merge into one. Of these curves G is the best. A decrease in the F-Si-Cl angle to 106° (J) leads to a worse curve than any of the 109 $\frac{1}{2}$ ° models. Three models (A, B and C) with larger angles were tried and of these model C (\angle F-Si-Cl = 110 $\frac{1}{2}$ °) is entirely satisfactory. From the way in which changes in the two shape parameters affect the scattering curves it is possible to fix the F-Si-Cl angle at 110 $\frac{1}{2}$ ° = 1° and the Si-Cl/Si-F ratio at 1.31 ± 0.02. The s values for the best model C and for models F and G are compared with the s_0 values in Table IV. The average s/s_0 ratio for model C leads to the following values:

Si-F = 1.55 ± 0.02 Å., Cl-F = 2.94 ± 0.03 Å., Si-Cl = 2.03 ± 0.03 Å., F-F = 2.50 ± 0.05 Å. These agree well with the corresponding radial distribution results, the largest discrepancy being a little more than 1% in the F-F term.

Discussion

The results on the three compounds are collected in Table VI together with distances observed in some related compounds.

TABLE VI
OBSERVED BOND DISTANCES

| | Si-Cl | Si-C | Si-F |
|--|----------------|----------------|----------------|
| Si(CH ₃) ₂ Cl ₂ | 1.99 ± 0.03 Å. | 1.83 ± 0.06 Å. | |
| Si(CH ₃)Cl ₃ | 2.01 ± 0.02 | | |
| SiF ₃ Cl | 2.03 ± 0.03 | | 1.55 ± 0.02 Å. |
| SiF ₄ ^a | | | 1.54 ± 0.02 |
| SiCl ₄ ^a | 2.02 ± 0.02 | | |
| Si(CH ₃) ₄ ^b | | 1.93 ± 0.03 | |
| Si ₂ (CH ₃) ₆ ^c | | 1.90 ± 0.02 | |
| SiC (carborandum) ^d | | 1.90 ± 0.005 | |
| Radius sum | | 1.94 | |
| Radius sum with electronegativity correction ^e | | 1.88 | |

^a L. O. Brockway and F. T. Wall, THIS JOURNAL, 56, 2373 (1934). ^b L. O. Brockway and H. O. Jenkins, *ibid.*, 58, 2036 (1936). ^c Ref. 2. ^d Ewald and Hermann, "Strukturbericht," 1931, p. 146. ^e V. Schomaker and D. P. Stevenson, THIS JOURNAL, 63, 37 (1941).

The silicon-chlorine distances in the new compounds are not much different from the values previously observed. This result is especially interesting in the case of SiF₃Cl where the Si-Cl bond length is the same as in SiCl₄. In the corresponding carbon compounds the C-Cl bond length in CF₃Cl is 0.05 Å. or 3% shorter than in CCl₄.⁵ This effect of the substitution of three fluorine atoms on the attachment of the remaining chlorine is apparently specific to the carbon compound since it does not occur in the silicon compound. The stabilizing effect of CF₃ groups on organic molecules is therefore not to be expected in analogous silicon compounds. The Si-F distance is the same in SiF₃Cl as in SiF₄.

The dimethyl silicon dichloride has the smallest Si-Cl distance yet observed but the uncertainty in the determination (0.03 Å.) is as large as the decrease below the most common value (2.02 Å.). The Si-C bond length, however, is apparently much shorter than in other silicon-carbon compounds. The value reported depends on the assumption of a regular tetrahedral angle between the two Si-C bonds. If this indeterminate angle is 115 or 120°, the bond distance is fixed at 1.87 Å. or 1.90 Å., respectively. Since an angle as large as 120° seems improbable the bond distance is probably less than that in Si₂(CH₃)₆ and certainly less than that in Si(CH₃)₄. Accordingly it appears that when a methyl group in Si(CH₃)₄ is substituted by Cl or Si(CH₃)₃ the Si-C bond length decreases; when a second Cl is substituted a further decrease takes place.

It is noted in the table that the covalent

radius sum for Si and C is 1.94 Å., or 1.88 Å. if an empirical correction is made for the electro-negativity difference; but neither of these values can be correlated with the several Si-C distances observed. If the repulsion between Cl and CH₃ 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(CH₃)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(CH₃)₂Cl₂ as compared with SiCl₄; 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(CH₃)₄, while the Si-Cl distances are not much different from the values observed in other silicon chlorides. The SiF₃ group in SiF₃Cl does not bind the chlorine more tightly than in SiCl₄ in contrast to the effect observed in CF₃Cl compared with CCl₄.

ANN ARBOR, MICHIGAN

RECEIVED OCTOBER 11, 1943

[CONTRIBUTION FOR THE CONTINENTAL CARBON COMPANY]

Hysteresis and the Capillary Theory of Adsorption of Vapors¹

BY LEONARD H. COHAN

Introduction

The Zsigmondy capillary theory^{1a-6} was one of the earliest of the theories⁷⁻¹³ which have been proposed to explain the adsorption of vapors on solids. It will be the purpose of this paper to reexamine, in the light of recent experiments, how satisfactory an explanation this theory offers.

The Zsigmondy capillary theory is based on the Kelvin equation

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

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, $\theta = 0^\circ$ 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

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- (1a) Lord Kelvin, *Proc. Roy. Soc., Edinburgh*, **7**, 63-68 (1870).
- (2) R. Zsigmondy, *Z. anorg. Chem.*, **71**, 356-377 (1911).
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- (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).

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 cases¹⁴ 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. Shereshefsky¹⁵ determined the rate of evaporation from capillaries only 2μ 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 Meyer¹⁶ determined σ and V in capillaries 2μ 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

- (14) A. G. Foster, *Trans. Faraday Soc.*, **28**, 645-657 (1932), also ref. 10, p. 1800, and ref. 8, p. 973.
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