CONTRIBUTION FROM THE U. S. BUREAU OF MINES CENTRAL EXPERIMENT STATION, AND THE DEPARTMENT OF CHEMICAL ENGINEERING, JOHNS HOPKINS UNIVERSITY]

Modifications of the Brunauer, Emmett and Teller Equation[1]

BY ROBERT B. ANDERSON[2]

The theory of multilayer adsorption as proposed by Brunauer, Emmett and Teller[3] has been applied extensively to physical adsorption isotherms. While the simple B. E. T. equation provides an excellent method of estimating surface areas,[4] it usually holds only for relative pressures of 0.05 to 0.40. In almost every case the amount adsorbed at relative pressures higher than 0.40 is less than that predicted by the simple B. E. T. equation. This discrepancy has been explained in three ways: (a) by assuming the heat of adsorption in the second layer to be less than the heat of liquefaction of the adsorbate[3,5,6]; (b) by assuming that the structure of the adsorbent is such that it will permit adsorption to only a finite number of layers[3]; and (c) by considering the effects of capillary condensation.[7] Isotherms in which capillary condensation probably occurs as characterized by flattening of the isotherm at sufficiently high relative pressures and usually by strong hysteresis will not be considered in this paper.

In studies of many isotherms involving the adsorption of a number of gases on presumably nonporous solids the author has observed that the simple B. E. T. equation can be fitted to the isotherms to relative pressures greater than 0.7 by multiplying the relative pressure by a constant that is less than one. In the present paper this constant is interpreted to mean that the heat of adsorption in the second to ninth layers is less than the heat of liquefaction. An equation of a similar type for adsorption isotherms on porous solids and a new type of equation for adsorption limited to n layers have been derived.

The isotherms used as examples were determined by conventional methods and the isotherms either have been described in the literature or will soon be published.

Modified B. E. T. Equation with Heat of Adsorption in Second and Next Several Layers Less than the Heat of Liquefaction.—In the following derivations the assumptions and development are the same as those of the B. E. T. equation[3] with the exception of the variation of the heat of adsorption in the second to ninth layers. One way that an equation containing such a factor as described in the introduction can be developed is to postulate that the heat of adsorption in the second to about ninth layer, $E_{2 \text{ to } 9}$, differs from the heat of liquefaction, E_L, by a constant amount d, and that the heat of adsorption is equal to the heat of liquefaction in the layers following these. Thus

$$E_{2 \text{ to } 9} = E_L + d \tag{1}$$

For convenience this quantity d will also be added to the heat of adsorption in the first layer E_1.

By the method of derivation of the B. E. T. equation[3] an approximate equation has been developed which is valid to relative pressures of about 0.7 to 0.8

$$\frac{V}{V_m} = \frac{cx'}{(1 - x')(1 + (c - 1)x')} \tag{2}$$

where V is the volume adsorbed, V_m the volume corresponding to a monolayer

$$c = \frac{a_1 b_2}{a_2 b_1} \exp (E_1 - E_L)/RT \tag{3}$$

in which $a_{1 \text{ and } 2}$ and $b_{1 \text{ and } 2}$ are rate constants for adsorption and desorption in the first and second layers, and

$$x' = \frac{pa_2}{b_2} \exp (E_L + d)/RT \tag{4}$$

where p is the pressure of the adsorbate. It is assumed that V becomes infinite at the liquefaction pressure of the adsorbate, $p = p_0$; however, under these conditions the first nine layers are insignificant compared with the total amount adsorbed and $d = 0$. In this limiting case

$$x' \longrightarrow x = p \frac{a_2}{b_2} \exp (E_L/RT)$$

and $x = 1$, and thus $x = p/p_0$. But for most of the isotherm equation 2 should be used, in which

$$x' = x \exp d/RT = kx \tag{5}$$

and

$$\frac{V}{V_m} = \frac{ckx}{(1 - kx)(1 + (c - 1)kx)} \tag{6}$$

In the linear form for testing the equation

$$\frac{x}{V(1 - kx)} = \frac{1}{V_m ck} + \frac{(c - 1)x}{cV_m} \tag{7}$$

In Fig. 1 is shown a plot of $x/V(1 - kx)$ against x for an isotherm of nitrogen at −195° on microscopic glass spheres prepared by the method of Bloomquist and Clark.[8] To show

---

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Physical Chemist, Bureau of Mines, Central Experiment Station, Pittsburgh, Pa.

(3) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

(4) Emmett, "Advances in Colloid Science," Vol. I, 1942, pp. 1–36; Emmett, *Ind. Eng. Chem.*, **37**, 639 (1945).

(5) Gans, Brooks and Boyd, *ibid.*, **14**, 396 (1942).

(6) Livingston, THIS JOURNAL, **66**, 569 (1944), pointed out that changes of heat of adsorption in second and subsequent layers from the heat of liquefaction will cause the relative pressure to be multiplied by a constant factor, and that for slight variations of this constant the linear plot of B. E. T. equation was not affected.

(7) Brunauer, Deming, Deming and Teller, *ibid.*, **62**, 1723 (1940).

(8) Bloomquist and Clark, *Ind. Eng. Chem., Anal. Ed.*, **12**, 61 (1940).

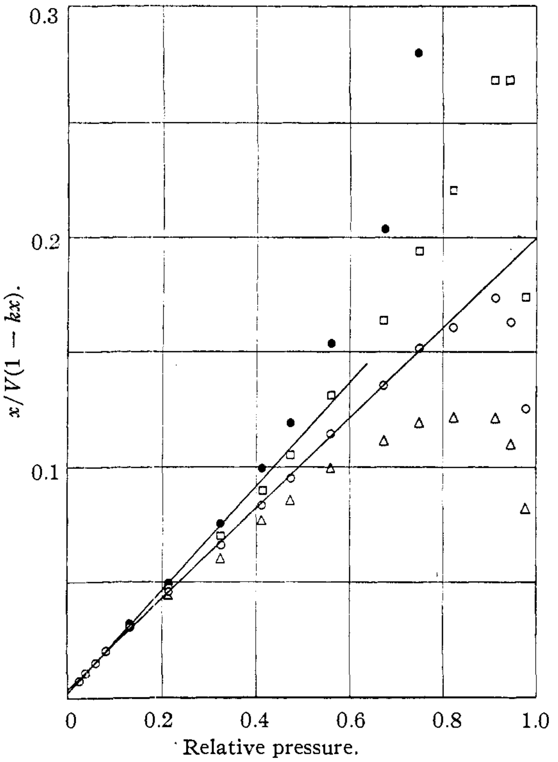

Fig. 1.—The influence of variation of the value of k on a plot of equation 7 on data for nitrogen on microscopic glass spheres at −195°, where the value of k of 1.0 is represented by ●, k = 0.85 by □, k = 0.715 by ○, and k = 0.55 by △.

variations of the linear plot with the value of k, the data are plotted for values of k of 1.0, 0.85, 0.715 and 0.55. The area as computed by the modified B. E. T. equation which best fits the data in the range 0.05 to 0.7 is $22.2m^2$ as compared with $20.9m^2$ by the simple B. E. T. equation. For this value of k (k = 0.715), the value of d is −53 cal.

In Fig. 2 are linear plots of nitrogen[9] and acetylene isotherms on Grade 6 Spheron carbon black at −195 and −78°, and nitrogen[9] and ammonia isotherms on Black Pearls 1 carbon black at −195 and −47°, respectively. In Fig. 3 is presented a similar plot for an isotherm of nitrogen on kieselguhr at −195°. In Table I are compared the values of area per gram and c for the isotherms shown in Figs. 1 to 4. In all cases the area per molecule was computed from the density of the liquid at that temperature.

Equation 6 has been fitted to isotherms of nitrogen, acetylene, ammonia and butane on various carbon blacks; nitrogen on glass spheres, kieselguhr and a kieselguhr–cobalt–thoria–magnesia Fischer–Tropsch catalyst; and nitrogen, water and n-propyl alcohol on TiO_2-I[5,10] within about 3% in the range of relative pressures of 0.05 to 0.7 or 0.8. The value of V_m as determined by equation 6 varied from 4 to 19% higher than that predicted by the simple B. E. T. equation. The surface area of TiO_2-I as calculated by equation 6 does not agree as well with the area determined from the heat of immersion experiments of Harkins and Jura[10,11] as the area from the simple B. E. T. equation; however, the area of the adsorbed film of water vapor which is actually measured by this method may be less than that of the titanium oxide, if the solid contains cracks and crevices of molecular size. From one isotherm to another the deviations between the values of c computed by equation 6 and the values of c by the simple B. E. T. equation showed no consistent variation; however, for any isotherm the values of $E_1 - E_L$ as computed by either equation are always of the same order of magnitude.

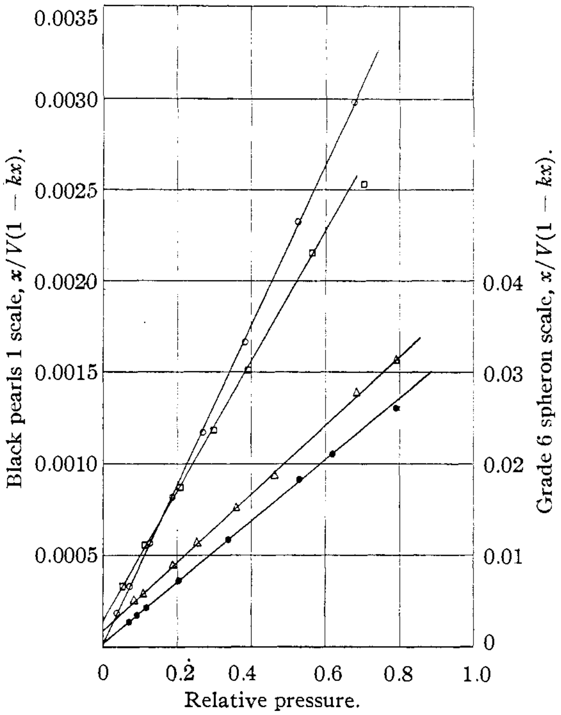

Fig. 2.—A plot of equation 7 of carbon black isotherms where ○ is nitrogen at −195° on Black Pearls 1 with k = 0.57, □ is ammonia on Black Pearl 1 at −47° with k = 0.70, ● is nitrogen at −195° on Grade 6 Spheron with k = 0.63 and △ is acetylene at −78° on Grade 6 Spheron with k = 0.63.

The agreement between surface areas as determined by the adsorption of different vapors on the same adsorbent is about the same for the simple and the modified B. E. T. equations. The deviations from the average surface area for two adsorbates on five different carbon blacks, three adsorbates on another carbon black, and two adsorbates on TiO_2-I averaged 3.6 and 2.9% for the simple and the modified B. E. T. equations.

---

(9) Emmett and Anderson, THIS JOURNAL, **67**, 1492 (1945).

(10) Harkins and Jura, *ibid.*, **66**, 1366 (1944).

(11) Harkins and Jura, *ibid.*, **66**, 919 (1944).

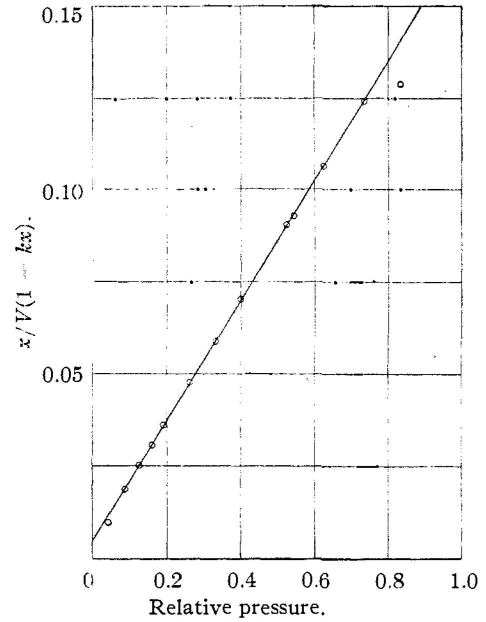

Fig. 3.—A plot of equation 7 of an isotherm of nitrogen on kieselguhr at −195° with $k = 0.6$.

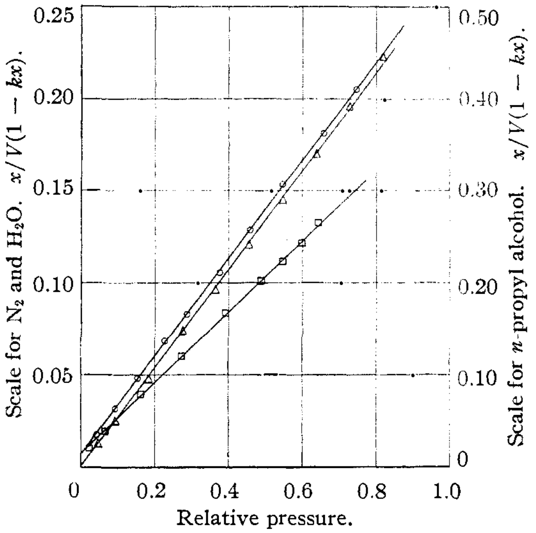

Fig. 4.—A plot of equation 7 of nitrogen, water and *n*-propyl alcohol isotherms on TiO_2-I in which ○ represents nitrogen at −195° with $k = 0.70$, □ represents water at 31° with $k = 0.75$ and Δ is *n*-propyl alcohol at 25° with $k = 0.17$.

The question of why the heat of adsorption in the second to tenth or so layers should be lower than the heat of liquefaction cannot be answered clearly. It is possible that d is the energy necessary to spread a mole of liquid into a layer eight or ten molecules in depth. An enthalpy of about 195 cal. is required to spread a mole of nitrogen into a monolayer against the normal surface enthalpy ($[\gamma - T(d\gamma/dT)]$, where γ is the surface tension) of liquid nitrogen at −195°. If this surface enthalpy is not furnished entirely in the formation of the first layer, and if the heat of adsorption in the second and next several layers excluding the surface enthalpy equals the heat of liquefaction, E_L, the heat of adsorption in these layers must be less than the heat of liquefaction. It should also be mentioned that equations of the type 1 to 6 can be set up using free energy of adsorption and liquefaction instead of enthalpies. These equations are more general, and constant k may be explained in terms of heat content, entropy or free energy. Thus, in terms of entropy, the entropy of adsorption in the second to ninth layers is more negative than the entropy of liquefaction, which indicates that the adsorbate in these layers is more ordered than the liquid phase.

Some unusual isotherms have been reported for *n*-propyl alcohol on presumably non-porous solids, in which the isotherms are quite flat with only slightly more than a monolayer adsorbed at relative pressures as high as 0.8.[5,6,10] Boyd[5] has postulated that the hydroxyl end of the alcohol is oriented toward the surface in the first layer. According to Boyd this leaves essentially a hydrocarbon surface for the adsorption of the second layer and hence a heat of adsorption in the second layer less than the heat of liquefaction. Equation 6 has been applied successfully to this type of isotherm. In Fig. 4 is given a plot of equation 7 on isotherms of *n*-propyl alcohol,[5] water[5] and nitrogen[8] on TiO_2-I with values of k equal to 0.17, 0.75 and 0.70, respectively. By using the cross-sectional area of the *n*-propyl alcohol molecule as

TABLE I

COMPARISON OF THE B. E. T. AND MODIFIED B. E. T. EQUATIONS

		k	M^2/g B. E. T.	M^2/g Mod.	c B. E. T.	c Mod.
Glass spheres	N_2 at −195°C.	0.715	20.9	22.2	72.2	55.1
Grade 6 Spheron	N_2 at −195[a]	.63	116.4	131.8	125.0	144.5
	C_2H_2 at −78	.65	110.0	130.9	33.4	34.3
Black pearls 1	N_2 at −195[a]	.57	942	998	245	438
	NH_3 at −47	.70	858	1015	27.8	42.6
Kieselguhr	N_2 at −195	.60	22.2	26.2	197.6	74.6
TiO_2-I	N_2 at −195[b]	.70	13.9	16.2	124.3	64.4
	H_2O at 31[c]	.75	12.4	14.7	48.6	32.6
	n-Propyl alc. at 25[c]	.17	[d]	13.6	[d]	>1000

[a] Ref. 9. [b] Ref. 10. [c] Ref. 5. [d] Boyd (ref. 5) used a type of the Langmuir equation to fit this isotherm.

computed from the liquid density, 27 sq. Å., the surface area obtained was in fair agreement with that obtained from the water isotherm (see Table I). The value of d is -1056 cal. Equation 6 has also been applied to n-propyl alcohol isotherms on barium sulfate and silicon dioxide for which the values of k were 0.3 and 0.6. In the derivation of equation 6 it was postulated that the heat of adsorption in the second to ninth layer is less than the heat of liquefaction, and not just in the second layer. However, when the value of k is small (less than 0.4), the adsorption is almost entirely confined to the first and second layers for values of relative pressure less than 0.7, and equation 6 is applicable to this type of isotherm.

A complete and more complicated equation than equation 6 has been derived which takes into consideration the fact that $d = 0$ after the r-th layer. In the derivation, equations 13 and 20 (which are developed later in this paper) are used and also the relation that can be derived from equation 13 that in the range where $d = 0$, $V_{n+1}/V_n = x$, where V_n and V_{n+1} are the volumes of gas adsorbed in the n-th and $n + 1$-th layers. From equation 20 the volume of gas adsorbed in the first r layers, $V_{1 \text{ to } r}$, and from equation 13 the volume of gas adsorbed in the $r + 1$-th to an infinite number of layers, $V_{r+1 \text{ to } \infty}$, can be evaluated.

$$\frac{V_{1 \text{ to } r}}{V_m} = \frac{ckx(1 - k^r x^r)}{(1 - kx)(1 + (c - 1)kx)} \tag{8}$$

$$\frac{V_{r+1}}{V_m} = \frac{ck^r x^{r+1}}{1 + (c - 1)kx} \tag{9}$$

$$\frac{V_{r+1 \text{ to } \infty}}{V_m} = \frac{ck^r x^{r+1}}{(1 + (c - 1)kx)(1 - x)} \tag{10}$$

From equations 8 plus 10

$$\frac{V_{\text{total}}}{V_m} = \frac{ckx}{(1 + (c - 1)kx)}\left[\frac{1 - k^r x^r}{1 - kx} + \frac{k^{r-1} x^r}{1 - x}\right] \tag{11}$$

In terms of the volume adsorbed as given by equation 6, V_6, equation 11 becomes

$$\frac{V_{\text{total}}}{V_6} = 1 + \frac{k^{r-1} x^r (1 - k)}{1 - x}. \tag{12}$$

The second term of equation 12 is not significant for relative pressures less than 0.7, when k has a value of 0.6 to 0.7 and r is greater than 7. Equation 12 has been applied to the nitrogen on glass sphere isotherm of Fig. 1, and the results are given in Fig. 5, where the solid line is the isotherm as given by equation 6 with $k = 0.715$, the circles are experimental points, and the squares and triangles are points computed by equation 12 with r equal to 9 and 10, respectively, and $k = 0.715$. With the nitrogen on kieselguhr isotherm of Fig. 3, equation 12 fits the data satisfactorily to the highest experimental point $x = 0.975$ with $k = 0.60$ and $r = 6$.

Recently Cassie[12] has published a statistical derivation of the B. E. T. equation. If the free energy of the liquid-like phase which follows the first layer is less than that of the liquid, for the next several layers, it can be shown that equation 13 of Cassie becomes of the form

$$\frac{V - V_1}{V} = p/p_0 \exp d/RT = k\, p/p_0$$

where V is the total amount adsorbed at pressure p and V_1 the amount of gas adsorbed in the first layer. This leads to an equation identical to equation 6 for the case of localized sites in the first layer.

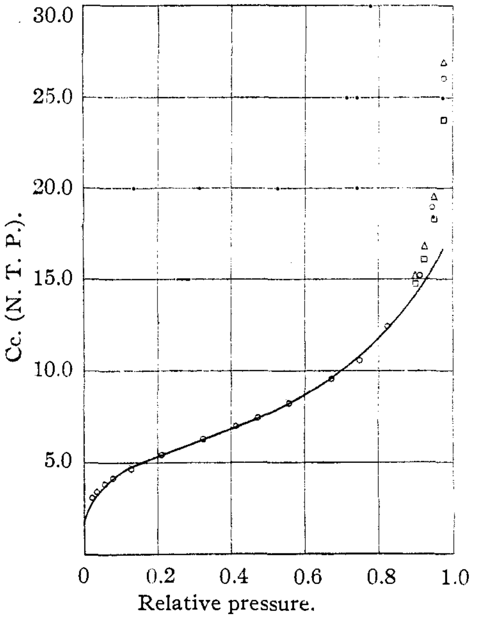

Fig. 5.—Adsorption of nitrogen on microscopic glass spheres at $-195°$, where the circles are experimental points. The solid line is a plot of equation 6 with $k = 0.715$. The triangles and squares are points as computed by equation 12 with r equal to 9 and 10, respectively, and $k = 0.715$. At relative pressures lower than 0.8 the triangles and squares fall upon the line.

Modified B. E. T. Equation for an Adsorbent in which the Surface Available to Each Subsequent Layer is Smaller.—For most porous substances it is probably closer to the actual conditions to assume that the surface area available to molecules in each subsequent layer decreases rather than to assume that the adsorption is limited to a finite number of layers. From the B. E. T. derivation it can be shown easily that the volume adsorbed in the n-th layer, V_n (this should not be confused with s_n, the area covered by stacks of n molecules in depth, as used in the B. E. T. derivation[3])

$$\frac{V_n}{V_m} = \frac{cx^n}{1 + (c - 1)x} \tag{13}$$

and the total adsorption

$$V = \sum_1^\infty V_n = \frac{V_m c}{1 + (c - 1)x}\sum_1^\infty x^n = \frac{V_m cx}{(1 - x)(1 + (c - 1)x)} \tag{14}$$

---

(12) Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

It is postulated that if the volume of adsorbate required to completely cover the n-th layer, A_n is less than V_m, the volume adsorbed in that layer at any relative pressure is decreased by the ratio of $A_n/V_m = q_n$. Thus

$$V_n = \frac{V_m c x^n q_n}{1 + (c - 1)x} \qquad (15)$$

$$\frac{V}{V_m} = \frac{c}{1 + (c - 1)x} \sum_1^\infty q_n x^n \qquad (16)$$

The simplest and only easily applicable case that has been found is the one in which the area available to each layer is a constant fraction, j, of the area available to the previous layer. Then $q_n = j^{n-1}$, and

$$V = \frac{V_m c}{1 + (c - 1)x} \sum_1^\infty j^{n-1} x^n = \frac{V_m c x}{(1 - jx)(1 + (c - 1)x)} \qquad (17)$$

In the linear form

$$\frac{x}{V(1 - jx)} = \frac{1}{V_m c} + \frac{(c - 1)x}{V_m c} \qquad (18)$$

It should be noted that this equation reduces to a form of the Langmuir equation when $j = 0$ and to the B. E. T. equation when $j = 1$. If the postulates of equation 6 hold in such systems, equation 18 would be modified to

$$\frac{x}{V(1 - jkx)} = \frac{1}{V_m ck} + \frac{(c - 1)x}{cV_m} \qquad (19)$$

where k varies from 0.6 to 0.7 for most adsorbates.

In Fig. 6 is a plot of equation 19 of a nitrogen isotherm at −195° on a steam-activated Grade 4 carbon black. The isotherm appears to be a composite of the usual "S" shape isotherm plus a charcoal-like isotherm due to capillaries developed in the activation. The value of jk equals 0.4, and by assuming k to equal 0.65, j is equal to 0.62. The value of V_m computed by equation 19 is 116.2 cc. compared with 117.0 cc. as estimated by the point B method.[13]

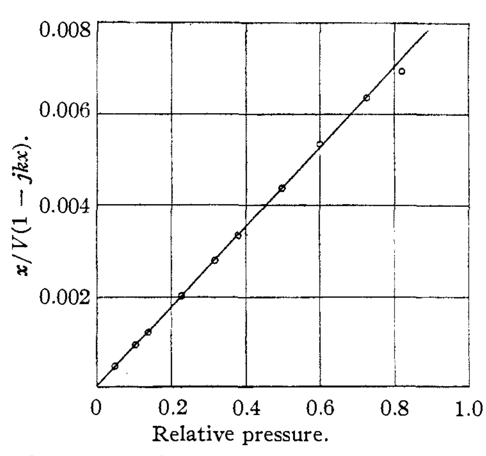

Fig. 6.—A plot of an isotherm of nitrogen on steam activated Grade 4 Spheron at −195° according to equation 19 with $jk = 0.4$.

Equation 19 has been applied to a variety of charcoal and activated carbon-black isotherms to which neither the simple B. E. T. or Langmuir equations can be fitted (however, the n-B. E. T. equation[3] can probably be fitted to these), and satisfactory agreement was usually obtained up to relative pressures of 0.7 or more. The values of kj varied from 0.1 to 0.4. In all cases the value of V_m corresponded to about the same point as chosen by the point B method.

From equation 13 it is possible to derive equation 20 for adsorption limited to n layers which is simple and perhaps has better properties than the equation of this type derived by Brunauer, Emmett and Teller.[3]

$$\frac{V}{V_m} = \frac{c}{1 + (c - 1)x} \sum_1^n x^n = \frac{cx(1 - x^n)}{(1 - x)(1 + (c - 1)x)} \qquad (20)$$

The equation reduces to the Langmuir equation when $n = 1$ and to the simple B. E. T. equation when $n = \infty$. When the relative pressure equals 1, V is equal to nV_m. The n-equation of B. E. T. reduces to $V_m c/(c + 1)$ for the case when $n = 1$ and $x = 1$, while equation 20 reduces to V_m under these conditions. Equation 20 seems to be more reasonable than the n-B. E. T. equation, for it is difficult to understand why the first layer should not be complete at $x = 1$, when the volume adsorbed on a free surface approaches infinity. Equation 20 is identical to the n-equation recently published by Pickett,[14] and the assumptions of the derivation are the same as used in Pickett's second method of derivation of the n-equation; that is, the distribution of molecules in the various layers is assumed to be the same as on a free surface with molecules in layers higher than n not included in the summation.

Acknowledgment.—The author wishes to thank Drs. P. H. Emmett and H. H. Storch for permission to use several unpublished isotherms. The use of free energy in the derivation of the B. E. T. equation was suggested by Drs. S. Weller and T. DeWitt.

Summary

It has been shown that the simple equation of Brunauer, Emmett and Teller[3] can be fitted to many physical adsorption isotherms in the range of relative pressures of 0.05 to 0.70, if the relative pressure is multiplied by a constant that is less than 1, usually varying between 0.6 and 0.7. The constant is interpreted to mean that the heat or free energy of adsorption in the second to tenth layers is less than the heat or free energy of liquefaction, or that the entropy of adsorption in these layers is more negative than the entropy of liquefaction. A similar equation containing an additional constant denoting the upper limit of the layers in which the heat, free energy or en-

---

(13) Emmett and Brunauer, *Trans. Faraday Soc.*, **59**, 1553 (1937).

(14) Pickett, *ibid.*, **67**, 1958 (1945).

tropy are different from those functions for the liquid has been fitted to isotherms in the range of relative pressures of 0.05 to 0.98. For porous solids equations have been presented for adsorption on solids in which the area available to each succeeding layer is less than the previous one. A new-type equation has been developed for adsorptions limited to n-layers which has better properties than the n-equation of B. E. T.[3]

PITTSBURGH, PA. RECEIVED DECEMBER 29, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Vapor Pressure–Viscosity Relations in Methylpolysiloxanes

BY DONALD F. WILCOCK

Liquid methylpolysiloxane mixtures, or silicone oils, exhibit unusually small changes in viscosity with temperature. Their viscosities at 100°F. are only about two and one-half times those at 210°F., while the corresponding factor for a petroleum oil of viscosity index 100 is about eight. This behavior of silicone oils suggested investigation of the relations between the viscous properties and the vapor pressure–temperature characteristics of those smaller polysiloxane molecules which may be separable as pure compounds.

The viscosities at several temperatures of a number of the linear and cyclic methylpolysiloxanes have been reported by Hurd,[1] and these same compounds were available for determination of vapor pressures. In addition the eight-silicon ring, hexadecamethylcyclooctasiloxane,[2] and the seven- to eleven-silicon chain compounds, hexadecamethylheptasiloxane to tetracosamethylundecasiloxane, were isolated and their vapor pressures, viscosities and densities were determined. Analysis of these data has yielded general equations relating vapor pressure to temperature and to the number of silicon-containing units. Similar equations relating viscosity to temperature and to the number of units have also been obtained. Estimates of the average size of the segmental unit of flow in the large polymeric chains likewise have been made by comparison of the viscous and vapor pressure properties.

For the sake of clarity and conciseness, the proper names of the methylpolysiloxane compounds will be abbreviated by use of a shorthand system of nomenclature based on the functionality of the basic silicon-containing units which appear in the molecules. The bifunctional repetitive unit, $(CH_3)_2SiO$, is termed a **D**-unit, and the monofunctional terminal group, $(CH_3)_3SiO_{1/2}$, is termed an **M**-unit. Using this system, simple cyclic molecules are written $\mathbf{D}_x$, and linear molecules are written $\mathbf{M}_2\mathbf{D}_{x-2}$, x being the total number of silicon containing units.

Experimental

The cyclic compound $\mathbf{D}_8$ was isolated by Patnode[3] by fractional distillation of the hydrolyzate of dimethyldichlorosilane. The linear compounds $\mathbf{M}_2\mathbf{D}_5$ to $\mathbf{M}_2\mathbf{D}_9$ were isolated by fractionally distilling through a packed column at reduced pressure the volatile portions from equilibrated[4] silicone oils. The fractions were carefully redistilled, but it was not possible to eliminate completely small amounts of the corresponding cyclic compounds which were present, because at distillation temperatures near 200° the boiling points of the cyclic compounds approach those of the corresponding linear compounds as the number of units is increased (see Fig. 2) The method of specific refraction[5] was used to determine the percentage of cyclic methylpolysiloxanes present as impurity, with the results shown in Table I. The compound $\mathbf{M}_2\mathbf{D}_5$ was not redistilled, and consequently was less pure than the others.

TABLE I

ANALYSIS OF NEW LINEAR METHYLPOLYSILOXANES

Compound	Density 20°	Refractive index at 20°	Specific ref.	Me:Si ratio	Wt. % chain
$\mathbf{M}_2\mathbf{D}_5$	0.911	1.3965	0.2640	2.234	82
$\mathbf{M}_2\mathbf{D}_6$	.913	1.3970	.2638	2.230	92
$\mathbf{M}_2\mathbf{D}_7$	.918	1.3980	.2629	2.212	96
$\mathbf{M}_2\mathbf{D}_8$	.925	1.3988	.2615	2.186	93
$\mathbf{M}_2\mathbf{D}_9$	.930	1.3994	.2604	2.165	91

Vapor pressures were determined by noting the boiling point of each compound at several pressures. A 14″ × 1/2″ jacketed distillation column packed with 3/32″ stainless steel helices was fitted just above the reflux condenser with a side tube connection leading to a McLeod gage capable of reading pressures as high as 50 mm. Pressure at the head of the column was regulated with a manostat capable of holding pressure within 0.1 mm. Pressures above 50 mm. were read from a manometer. Each compound was placed in the still pot and slowly distilled at constant pressure until the vapor temperature at total reflux was within 0.1° of the temperature during partial takeoff. The temperature was then noted and the process repeated at other pressures. The experimental values are summarized in Table II.

Kinematic viscosities were determined in modified Ostwald pipet viscometers at 100 ± 0.1°F. and 210 ± 0.1°F., with a precision of 0.5%. Absolute viscosities were calculated from the kinematic values and the densities. Densities were determined in a 4.5 cc. dilatometer at 20 ± 0.1° with a precision of 0.05%. Refractive indices were measured with an Abbe-type refractometer at 20 ± 0.1° using the sodium D-line.

Vapor Pressures

The vapor pressure–temperature curves for both the cyclic and linear series of compounds are plotted in Fig. 1. These log p vs. $1/T$ curves are straight lines for both the linear and cyclic com-

---

(1) Charles B. Hurd, THIS JOURNAL, **68**, 364 (1946).

(2) For a discussion of organosilicon nomenclature, see R. O. Sauer, *J. Chem. Ed.*, **21**, 303 (1944).

(3) Winton Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 358 (1946).

(4) The process of equilibration, see ref. 3, involves an equilibrium rearrangement of the **M** and **D** units into a system comprising linear polysiloxanes using sulfuric acid as a catalyst.

(5) Sauer, THIS JOURNAL, in press.