idue, the direction of change of composition of the residue alters abruptly in the direction of the benzene corner, so that when eventually the last trace of alcohol is removed, the binary mixture produced is much richer in benzene than the original mixture. From this binary mixture both benzene and carbon tetrachloride can (theoretically) be obtained by distillation, since the binary mixture benzene–carbon tetrachloride shows neither minimum nor maximum on the boiling point curve. It appears, therefore, that in the quadrilateral area pure benzene, pure carbon tetrachloride and the low boiling azeotrope can be obtained by fractionation. In addition, however, certain of the middle fractions would tend to approximate to the higher boiling azeotrope of benzene–alcohol but, as with the triangular area, it is doubtful whether in practice any of this binary azeotrope, uncontaminated by carbon tetrachloride, would be obtained, because of the strong curvature of the tie-lines around the trough.

The above predictions were borne out in practice by our distillation experiments.

Summary

The boiling temperatures, under constant pressure, of the binary systems alcohol–benzene, alcohol–carbon tetrachloride, and benzene–carbon tetrachloride, as well as those of the ternary system alcohol–benzene–carbon tetrachloride, have been investigated. The equilibrium concentrations of liquid and vapor for the above systems have been determined, with an accuracy of 0.3 weight per cent.

It is shown that the system benzene–carbon tetrachloride does not exhibit an azeotropic minimum on its boiling point curve. An improved barostat is described.

The liquid–vapor composition diagram is discussed and the course of distillation predicted. The course of distillation has been verified qualitatively by experiment.

WINNIPEG, CANADA RECEIVED OCTOBER 7, 1947

[CONTRIBUTION FROM THE BUREAU OF MINES, DEPARTMENT OF THE INTERIOR]

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

BY ROBERT B. ANDERSON[2] AND W. KEITH HALL[2]

The simple Brunauer, Emmett and Teller equation[3] (hereafter abbreviated to B.E.T.) has been useful in the estimation of surface areas from physical adsorption isotherms. This equation will fit satisfactorily experimental data for almost all isotherms except those of Type I of Brunauer, Deming, Deming and Teller[4] in the relative pressure range of 0.05 to 0.40. Several modifications of the simple B.E.T. equation have extended the range of applicability. In most cases the adsorbent structure is pictured as a series of parallel plates which will permit the adsorption of only n-layers from each side. An n-equation derived by B.E.T.[3] and Hill[5] extends the fit to higher relative pressures for most isotherms, but it is somewhat difficult to apply to experimental data.[6] Brunauer, Deming, Deming, and Teller[4] derived a more elaborate n-equation in which the heat of adsorption of the last layer adsorbed in a condenser plate capillary was higher than the heat of liquefaction. Although this equation can be fitted to the entire isotherm, its application is too difficult to be of any practical value as a method of characterizing isotherms.

Pickett[7] presented a simpler type of n-equation than that of B.E.T., one which is more easily applicable to adsorption data and probably fits over a greater range. The simplest derivation of this equation assumes that the volume of gas adsorbed in any layer is independent of the molecules adsorbed in higher layers; whereas, the n-equation of B.E.T.[3] implies that adsorption of molecules in higher layers stabilizes the molecules in underlying layers.

Recently, Anderson[8] suggested that the parallel plate type of pore structure is probably not a good physical picture of most porous adsorbents. A pore structure in which the area available to each subsequent layer is less than the area of the underlying layer is probably a better physical picture. In this paper it was also shown that for isotherms of finely divided, presumably non-porous solids such as carbon black, titania, etc., the modified B.E.T. equation could be fitted to the range of relative pressure of 0.05 to 0.7 by assuming the free energy of adsorption in the several layers after the first to be less than the free energy of liquefaction.

In the present paper, an equation embodying the same assumptions is derived in a manner similar to that of the B.E.T. equation. It can be satisfactorily fitted to isotherms of Type I and those approaching Type I by assuming the free energy of adsorption in the second and subsequent layers

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

[4] Brunauer, Deming, Deming and Teller, *ibid.*, **62**, 1723 (1940).

[5] Hill, *J. Chem. Phys.*, **14**, 263 (1946).

[6] Joyner, Weinberger and Montgomery, THIS JOURNAL, **67**, 2182 (1945).

[7] Pickett, *ibid.*, **67**, 1958 (1945).

[8] Anderson, *ibid.*, **68**, 686 (1946).

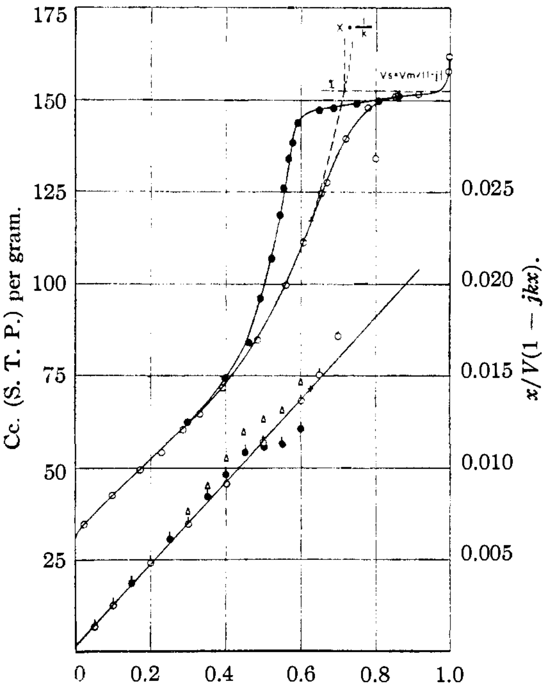

Fig. 1.—Adsorption isotherm and linear plot of equation 4 of nitrogen on iron oxide gel 47 C at −195°, where ○ and ● represent the adsorption and desorption isotherm, ϕ represents the linear plot of the adsorption isotherm with $jk = 1$, and ⧭ and △ are linear plots of the desorption isotherm with $jk = 1.1$ and 1.2, respectively. The plus sign indicates where the data begin to deviate from the linear plot.

equal to that of liquefaction. The same equation can be fitted to Type IV isotherms,[4] which flatten below relative pressures of 0.85 by assuming the free energy of adsorption to be greater than that of liquefaction. This equation was used to integrate the equation of Kistler[9] for the latter type of isotherms. The areas computed with Kistler's equation were at least of the same order of magnitude as areas from the modified B.E.T. equation presented here or the simple B.E.T. equation.

In this paper adsorption in a capillary is assumed to occur in the same manner as on a free surface with capillary forces causing the pores to fill at relative pressures less than 1. Isotherms used as examples in this paper were determined by conventional volumetric and gravimetric methods, and either have been or will soon be described in the literature.

Derivation of a Modified B. E. T. Equation and Application to Type IV Isotherms.—The derivation follows that of the original B.E.T. equation[3] in which

$$V/V_m = \sum_0^\infty i s_i \Big/ \sum_0^\infty s_i \qquad (1)$$

where V is the number of adsorbed gas molecules, V_m the number of molecules required to form a monolayer, and s_i is the number of sites covered with stacks i molecules high. In pore systems in which the area available to each layer is less than that of the layer underneath, it is assumed that at any relative pressure the volume adsorbed in the i-th layer is equal to the amount that would be adsorbed in this layer on a plane surface multiplied by A_n/V_m where A_n is the number of molecules required to fill the n-th layer. Although the relationship of A_n to V_m for any postulated type of pore is a function too complicated to give a simple summation of equation (1), it may be satisfactorily approximated in many cases by assuming $A_n/A_{n-1} = j$, where j is a constant less than 1. Since the surface area is defined as the area occupied by the first layer, the j correction will not be applied to it. This results in the relationship[10] that $s_i = s_0 c j^{i-1} x^i$. Thus

$$\frac{V}{V_m} = \frac{c s_0 \sum_1^\infty i j^{i-1} x^i}{s_0\left(1 + c\sum_1^\infty j^{i-1} x^i\right)} = \frac{cx}{(1 - jx)[1 + (c - j)x]} \qquad (2)$$

where, as in the simple B.E.T. equation, x is identified as p/p_0. At $x = 1$, almost all of the pores should be filled and since c is usually 5 to 100 and $1 > j > 0$

$$V/V_m = c/(1 - j)(1 - j + c) \cong 1/(1 - j) \cong V_s/V_m \qquad (3)$$

where V_s is the number of adsorbate molecules required to fill the pore system.

If the free energy of adsorption in the second and subsequent layers differs from the free energy of liquefaction by an equal amount d, then following the derivation by Anderson[8]

$$\frac{V}{V_m} = \frac{ckx}{(1 - jkx)[1 + (c - j)kx]} \qquad (4)$$

where $k = \exp d/RT$. The energy terms in the exponents of the equations for c and k are free energies of desorption and are opposite in sign to free energies of adsorption. Thus, if d is positive (k greater than 1), the free energy change in adsorption in the second and subsequent layers is more negative than the free energy of liquefaction, and the pores of the adsorbent should fill at relative pressures less than 1. In equation 4, almost all of the pores will be filled at $x = 1/k$. In systems of small pores the free energy of adsorption in second and subsequent layers may be expected to be less than that of liquefaction, since surface

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(9) Kistler, Fischer and Freeman, *ibid.*, **65**, 1909 (1943).

(10) This relationship is not obvious but can be shown in the following manner: let V_i be the number of sites covered by i or more layers; then, for adsorption on a plane surface, $V_i = \sum_i^\infty s_i = s_i/(1 - x)$, and $V_i/V_{i-1} = s_i/s_{i-1}$. For adsorption in a capillary the value of V_i/V_{i-1} should be multiplied by j, and hence the ratios s_i/s_{i-1} should also be multiplied by j. Thus, $s_i'/s_{i-1}' = js_i/s_{i-1} = jx$ where the primes indicate the values of s_i and s_{i-1} for adsorption in a capillary. In the rest of the derivation the primes will be omitted.

area decreases as the amount adsorbed increases. Equation 4 is similar to the equation derived previously[8] using the same assumptions as Pickett,[7] except that $(c - j)$ appears in the second term in the denominator instead of $(c - 1)$. The difference is negligible except for values of c near 1 and values of j near zero.

Equation (4) can be fitted to adsorption data by plotting $x/V(1 - jkx)$ against x with the constant jk varied to give the best straight line, and $1/V_m$ = slope + kj (intercept). To simplify computation, the volume adsorbed was read from the isotherms in intervals of 0.05 relative pressure unit. Tables of $x/(1 - jkx)$ were prepared, with corresponding values of x and for values of jk in intervals of 0.05 in the range of 0.00 to 1.40. Then, in making the modified B.E.T. plots, it was necessary only to divide the values in these tables by the volume adsorbed. Since fairly close approximations of j and k can be made from the isotherms, usually only one to three plots were necessary to establish the best value of the product jk. For evaluation of constant c, the adsorption equation was solved for c with $V = V_m$ in terms of x_m, the relative pressure at which $V = V_m$.

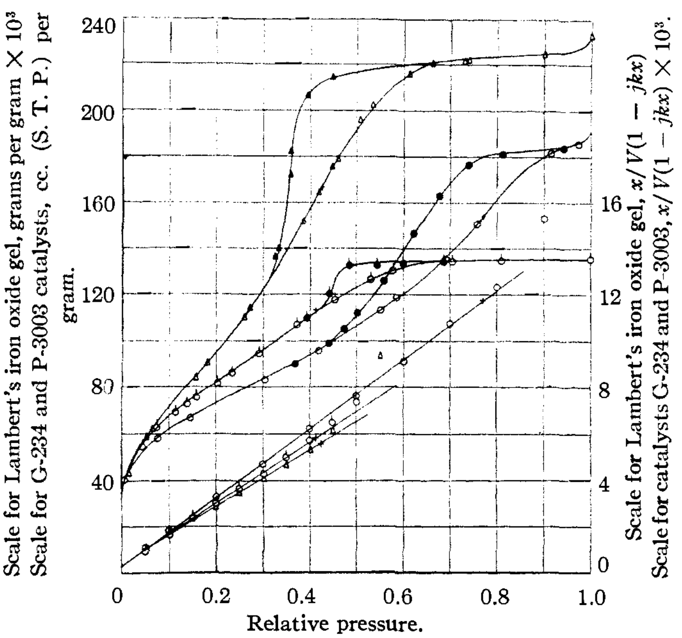

Fig. 2.—Isotherms and linear plots of benzene on Lambert's iron oxide gel at 50° with jk = 1.30; △, nitrogen on Fe_2O_3-CuO-K_2CO_3 Fischer–Tropsch catalyst P 3003 at −195° with jk = 0.90, ⌽, and nitrogen on Fe_2O_3-CuO-CaO-Kieselguhr Fischer–Tropsch catalysts G 234 with jk = 0.75, ○. Desorption points are solid, and the plus signs indicate where the data begin to deviate from the linear plot.

TABLE I

DATA FOR TYPE IV ISOTHERMS

Adsorbent Fe_2O_3 gels	Adsorbate	T, °C.	V_m[a]	Area sq. m./g.	V_s[a]	c	jk		k	Point +	$\bar{d}$[b] Å.	Area[c] sq. m./g.	$\bar{d}$[c] Å.
47C[d]	N_2	−195	44.1	193.0	152.5	42.2	1.00	0.711	1.41	0.63	49.0		
110C[e]	N_2	−195	39.3	172.1	124.7	54.4	1.05	.685	1.53	.55	44.9		
10K[d]	N_2	−195	38.5	168.9	129.0	56.6	1.00	.701	1.43	.65	47.4		
Lambert's[f]	C_6H_6	+ 40	0.0834	197.2	0.236	24.2	1.30	.647	2.01	.43	55.2		
	C_6H_6	+ 50	0.0773	185.3	0.221	17.3	1.30	.650	2.00	.43	55.9		
Fe_2O_3–CuO gels													
P 3003[g]	N_2	−195	74.8	327.5	134.0	17.6	0.90	.442	2.06	.43	25.4		
G 234[h]	N_2	−195	68.2	289.7	186.8	37.3	.75	.635	1.18	.77	38.8		
Porous glass[i]													
3	N_2	−195	49.7	217.7	120.5	125.8	.80	.587	1.39	.68	34.3		
3	A	−195	52.9	201.8	142.6	29.6	.95	.629	1.51	.62	35.3		
3	n-C_4H_{10}	0	14.5	125.8	40.0	5.7	1.00	.638	1.57	.55	54.4	237.9	31.1
5	N_2	−195	66.1	289.6	107.0	44.5	0.75	.382	1.96	.48	22.9		
5	n-C_4H_{10}	0	20.3	175.7	36.3	4.2	.95	.433	2.19	.43	34.8	307.9	19.9
7	N_2	−195	59.5	260.5	136.0	63.9	.85	.562	1.51	.65	32.3		
7	A	−195	57.9	221.0	159.3	25.2	1.00	.636	1.57	.65	36.0		
7	n-C_4H_{10}	0	15.2	131.6	48.9	6.3	1.20	.690	1.74	.55	63.6	230.5	36.3
Silica gels													
SiO_2 catalyst[j]	N_2	−195	79.7	349	590	95.8	0.90	.865	1.04	.63	105.0		
Aerogel[k]	N_2	−195	255.9	1120	1298	60.2	0.70	.804	0.87	.72	118.0		

[a] All data for V_m and V_s expressed as cc. (S. T. P.)/g. except Lambert's which are expressed as g. of adsorbate per gram. [b] Average pore diameter calculated from equation of Emmett and DeWitt[16] and equations (10) and (11) in the text. [c] Area and average pore diameter for n-butane isotherms assuming the cross-sectional area of butane to be 1.75 times the value of 32.1 Å.[2] [d] Ref. 11. [e] Unreduced iron Fischer–Tropsch catalyst similar to 10K. [f] Ref. 12. [g] P 3003, iron–copper–potassium carbonate (100:10:0.5) Fischer–Tropsch catalyst. [h] German iron Fischer–Tropsch catalyst (Fe: Cu:CaO:Kieselguhr = 100:2.5:10:15) prepared by Ruhrchemie. [i] Ref. 13. [j] Almost pure SiO_2 gel. [k] Sample from Prof. D. B. Keyes.

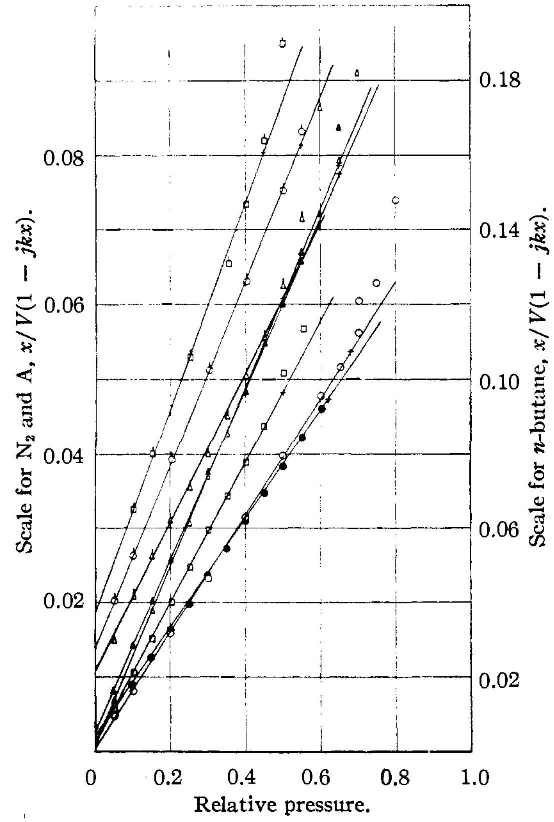

Fig. 3.—Linear plots of adsorption isotherms on porous glass where ○, ● and ○̍ represent nitrogen, argon and *n*-butane on 0.253 g. of porous glass 3, □ and □̍ represent nitrogen and *n*-butane on 0.157 g. of porous glass 5, and △, ▲ and △̍ represent nitrogen, argon and *n*-butane on porous glass 7. The plus mark indicates the highest point at which the points fall on the straight line. Nitrogen and argon isotherms were determined at −195° and *n*-butane at 0°.

Application of equation (4) to the nitrogen adsorption and desorption isotherms of iron oxide gel catalyst 47C[11] is shown in Fig. 1. For the adsorption isotherm, the linear plot is satisfactory to the point marked +, which is about the point of inflection of the adsorption branch. The constants of the equation are $V_m = 44.1$ cc. and $jk = 1$, in this case the linear plot being identical to that of the simple B.E.T. equation. From equation (3) evaluated with $V_s = 151.5$, $j = 0.7111$ and thus $k = 1.408$. The isotherm calculated for relative pressures higher than the + mark is shown by the broken curve. This curve, which appears to be an extrapolation of the adsorption isotherm below +, intersects V_s at a relative pressure equal to $1/k$. This is useful in approximating the choice of jk, since j can be estimated from equation (3) assuming V_m to occur at $x = 0.1$.

In Fig. 1, equation (4) has also been applied to the desorption isotherm. The plots for the best choices of jk, 1.1 and 1.2, are not satisfactory, indicating the equation is not applicable to the desorption branch.

Equation (4) has been applied to the adsorption isotherms of nitrogen, argon, butane, and benzene on several ferric oxide gels and porous glasses with equal success. The equation has been fitted satisfactorily to all isotherms of this type which flatten below a relative pressure of 0.85. Isotherms of nitrogen on ferric oxide–copper oxide–potassium carbonate Fischer–Tropsch catalyst P3003, German ferric oxide–copper oxide–calcium oxide–kieselguhr catalyst 234, and benzene on ferric oxide gel of Lambert[12] and the corresponding plots of equation (4) are presented in Fig. 2. In Fig. 3 are linear plots of data for adsorption isotherms of nitrogen, argon, and butane on porous glasses 3, 5, and 7.[13] Data for the application of equation (4) to the isotherms shown in Figs. 1, 2, and 3 and several similar isotherms are summarized in Table I. Included in the table are data for two isotherms of nitrogen on silica gels which flatten above 0.85. These data, as well as data on average pore diameters, will be described in later sections. The value of V_m computed from equation (4) will vary slightly from the V_m computed from the simple B.E.T. equation, being higher for jk lower than 1 and lower for jk higher than 1. Since the difference is less than 10% in all cases, V_m from the simple B.E.T. equation has not been included. With the exception of the two silica gel isotherms, equation (4) could be satisfactorily fitted to the adsorption isotherm from relative pressures of 0.05 to the point of inflection, but the equation could not be fitted to the desorption isotherm.

The physical interpretation of equation (4) is that the capillary forces shift the p_0 value of the adsorbate from p_0 to p_0/k, and at a relative pressure of $1/k$ all, or almost all, of the pores are filled. The lack of fit above the point marked + may be due to the rather crude approximation of the assumptions of equation (4) to the pore structure of the adsorbent. Some isotherms such as those shown in Figs. 1 and 2 flatten and then rise again at high relative pressures. This is very probably due to a small fraction of very large pores. The value of V_s in these cases is taken as the point where the isotherm begins to rise again.

For isotherms which flatten above relative pressures of 0.8 or 0.85, equation (4) does not fit data satisfactorily to the point of inflection as in Fig. 4, although the data can usually be fitted to relative pressures of 0.7. This is interpreted as indicating that in systems of larger pores it is not permissible to assume the capillary forces effective in all layers, but that these forces become effective only in the third or higher layers. Equations embodying the assumption that the free energy of adsorption becomes less than that of

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[11] Hofer, Peebles and Dieter, THIS JOURNAL, **68**, 1953 (1946).

[12] Lambert and Clark, *Proc. Roy. Soc.* (*London*), **A122**, 497 (1929).

[13] Emmett and Cines, *J. Phys. Colloid Chem.*, **51**, 1248 (1947).

liquefaction in the third or higher and subsequent layers can be derived, but the difficulty in application to data is too great for them to be of interest as a simple method of characterizing isotherms with a few constants. Examples of isotherms of this type are those of the silica gel catalyst and a silica aerogel, as shown in Fig. 4. The values of k were 1.04 and 0.87, respectively, for these isotherms. This suggests a transition in systems of large pores of the values of k from greater than 1 as characteristic of small pores to values of k less than 1 as observed for non-porous solids. Kistler[9] has postulated the structure of aerogels to be a "felt" of fibers. Hence, when the surface is covered with only two or three layers it may act as a non-porous adsorbent.

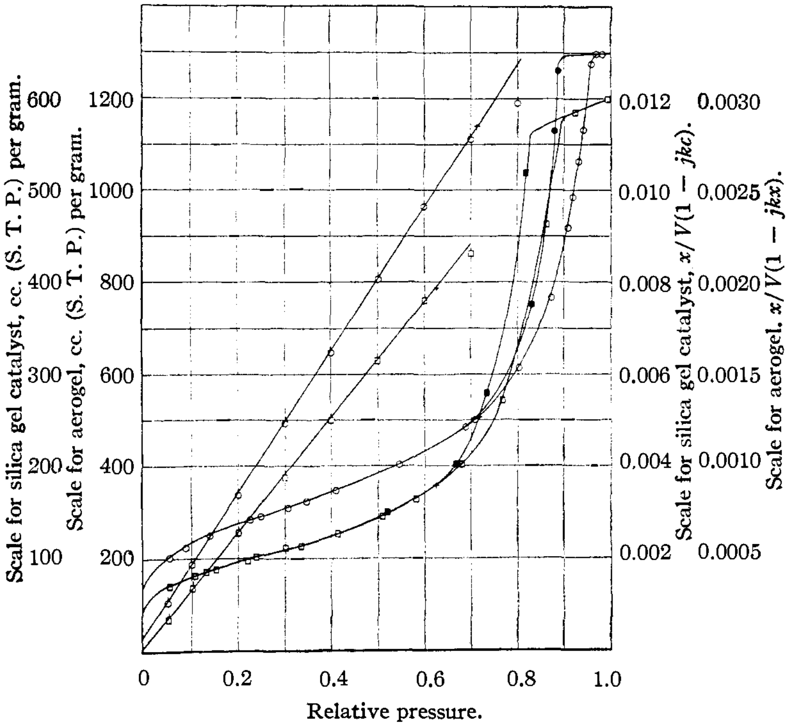

Fig. 4.—Adsorption isotherms and linear plots of nitrogen at −195° on silica catalyst □ and on aerogel O. Desorption points are solid and points of linear plot have tails. The plus sign indicates where data begin to deviate from linear plot.

Kistler[9] presented an equation for determining surface area without the assumption of an area per adsorbed molecule. In this equation, the free energy change in completely filling a system of capillaries covered by a monolayer (as computed from the adsorption isotherm) was equated to the decrease in surface area per gram, ΔA, times the normal surface tension of the liquid, σ. That is

$$\Delta A = -(RT/M\sigma)\int_0^{W(x=1)} \ln x \, \mathrm{d}W \qquad (5)$$

where W is the total weight adsorbed minus the weight of adsorbate in the first layer in grams per gram of adsorbent. W was computed by subtracting a Langmuir-type isotherm fitted to points at low relative pressures from the adsorption isotherm, and the integral was evaluated graphically. It should be noted that: (a) equation 5 is only applicable to porous adsorbents in which all of the pores are completely filled at $x = 1$, (b) identification of the surface free energy of the first layer with the normal surface tension of the liquid may be a poor assumption, and (c) this equation does not confirm or deny multilayer adsorption.

Equation 5 may be written as

$$\Delta A = \Delta F_n'/\gamma \qquad (6)$$

where $\Delta F_n'$ is the free energy change in the process of going from a system of pores covered with a monolayer to a completely filled capillary system, and γ is the surface free energy, which is not necessarily equal to the normal surface tension. In equation 7, $\Delta F_n'$ is expressed in terms of ΔV, the volume of gas adsorbed in the second and subsequent layers in cc. (S.T.P.) per gram, that is, $\Delta V = V - V_1$, where V_1 is the volume adsorbed in the first layer. The variables of the integration have also been changed.[14]

$$\Delta F_n' = -\frac{RT}{22{,}400}\int_0^{V(x=1)} \ln x \, \mathrm{d}\Delta V = \frac{RT}{22{,}400}\int_0^1 \Delta V \, \mathrm{d} \ln x \qquad (7)$$

Thus for Type IV isotherms which flatten below relative pressures of 0.85 (isotherms to which equation (4) is applicable), equation (7) may be evaluated with

$$\frac{V_1}{V_m} = \frac{\sum_1^\infty s_i}{\sum_0^\infty s_i} = \frac{ckx}{1 + (c - j)kx} \qquad (8)$$

Equations (4) and (8) may be substituted into the last term of equation (7), and the integral evaluated to point I of Fig. 1 ($x = 1/k$) with $\Delta V = V - V_1$ and from $x = 1/k$ to $x = 1$ with $\Delta V =$

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[14] This transformation is made as follows

$$\int_0^{V(x=1)} \ln x \, \mathrm{d}\Delta V = -\int_0^1 \Delta V \, \mathrm{d} \ln x + \Delta V \ln x \Big|_{x=0}^{x=1}$$

The upper limit of the second term of the right side of the equation is zero, and since at very low relative pressures $\Delta V = ckx$,[2] equation 4 minus equation 8, the indeterminate lower limit can be shown to be zero.

Table II

Data for Kistler's Equation

Adsorbent[a] Fe$_2$O$_3$ gels	Adsorbate	T., °C.	$\Delta F_n'$[b] ergs × 10^{-7}	Area, sq. m./g.			σ[c]	γ[d]
				$\frac{\Delta F_n'}{\sigma}$	from V_m S	$S(1 + j)/2$		
47C	N$_2$	−195	2.58	307.9	193.0	165.0	8.4	15.6
110C	N$_2$	−195	2.31	275.7	172.1	145.0	8.4	15.9
10K	N$_2$	−195	2.28	265.0	168.9	143.5	8.4	15.9
Lambert's	C$_6$H$_6$	40	6.10	232.7	197.2	162.4	26.3	37.5
		50	5.90	235.0	185.3	152.6	25.1	38.6
Fe$_2$O$_3$–CuO gels								
P-3003	N$_2$	−195	2.32	276.0	327.5	236.0	8.4	9.8
G-234	N$_2$	−195	2.44	290.8	298.7	244.1	8.4	10.0
Porous glasses								
3	N$_2$	−195	1.91	227.2	217.7	172.7	8.4	11.1
3	A	−195	2.48	166.5	201.8	164.3	14.9	15.1
3	n-C$_4$H$_{10}$	0	2.49	166.4	(237.9	194.7)	14.9	(12.8)
					(125.8	103.0		(19.8)
5	N$_2$	−195	1.66	197.4	289.6	200.0	8.4	8.3
5	n-C$_4$H$_{10}$	0	2.24	149.6	(307.9	220.5)	14.9	(10.2)
					(175.6	125.8)		(17.8)
7	N$_2$	−195	2.29	272.0	260.5	203.2	8.4	11.3
7	A	−195	2.88	193.0	227.0	184.5	14.9	15.5
7	n-C$_4$H$_{10}$	0	3.50	234.3	(230.5	194.6)	14.9	(18.0)
					(131.6	111.1)		(31.5)

[a] Adsorbents described in Table I. [b] Computed from equation 9. [c] Normal surface tension of liquid in ergs/sq. cm. [d] Surface free energy of the first layer of adsorbate in ergs/sq. cm., computed by dividing $\Delta F_n'$ by $S(1 + j)/2$.

$V_s - V_m$. This gives

$$\Delta F_n' = \frac{2.3\ RT\ V_m}{22{,}400}\left\{\frac{j}{c - j}\log_{10}(1 + c - j) + \log_{10}(1 - j) - \frac{j}{1 - j}\log_{10} k\right\} \quad (9)$$

Data for the application of equation (9) to isotherms of Table I are given in Table II. Surface areas, ΔA, computed from the free energy divided by normal surface tension were usually larger than S, the area computed from V_m. The decrease in area, ΔA, is the area of the interface between the first and second layer. As an approximation this can be taken as half the sum of the areas of the first and second layers, which is $S(1 + j)/2$; however, this area gives poorer agreement with ΔA than S. A small part of the discrepancy is due to the fact that equation (4) predicts a larger volume adsorbed than that of the actual isotherm in the vicinity of point I as shown in Fig. 1. In all cases the areas predicted from equations (4) and (9) are of the same order of magnitude.

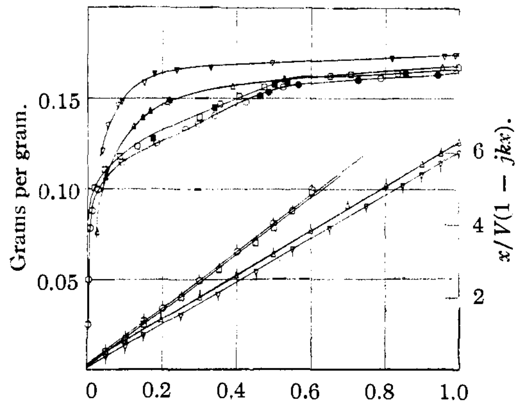

Fig. 5.—Adsorption isotherms and linear plots of ethanol and benzene on Lambert's silica gel, where □ and O indicate ethanol at 50 and 60°, respectively, and ▽ and △ benzene at 15.2 and 70°, respectively. Solid points indicate desorption, and points on linear plots have tails.

The surface free energy, γ, was computed by

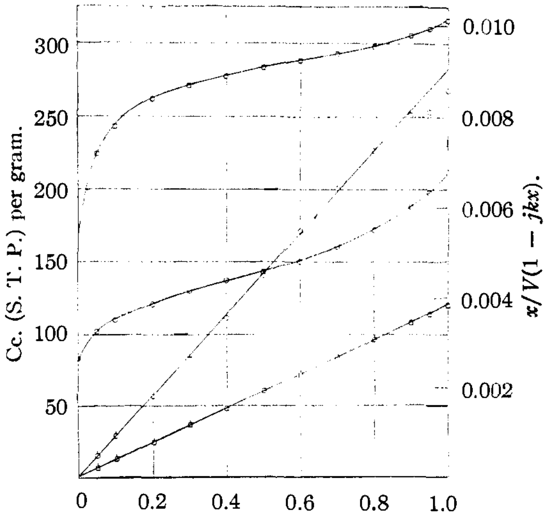

Fig. 6.—Adsorption isotherms and linear plots of nitrogen on charcoals PC1-1042, □, and PC1-1042 degassed O. Points of linear plots have tails.

TABLE III

DATA FOR TYPE I ISOTHERMS

Adsorbent	Adsorbate	T, °C.	V_m[a]	Area sq. m./g.	V_s[a]	jk	j	$\bar{d}$ Å.[b]
Lambert's silica gel[c]	C_6H_6	15	0.1680	391.3	0.1744	0.05	0.038	20.3
		40	.1661	394.1	.1732	.05	.041	20.3
		50	.1645	394.1	.1730	.05	.051	20.6
		70	.1616	394.1	.1680	.05	.038	20.5
	C_2H_5OH[e]	50	.1285	393.0	.1662	.4	.232	22.0
		60	.1260	386.5	.1662	.4	.242	22.5
Charcoal[d]								
PCI-1042	N_2	−195	269.0	1180	316.0	.17	.14	16.5
PCI-1042 (degassed)	N_2	−195	110.5	484	212.0	.45	.48	27.3
NS_5	N_2	−195	413.5	1810	418.0	.00	.01	14.2
NS_5 (degassed)	N_2	−195	266.0	1165	293.0	.10	.09	15.9

[a] Data of V_m and V_s expressed as grams adsorbate per gram for isotherms of Lambert[13] and cc. (S. T. P.)/g. for isotherms of Anderson and Emmett.[15] [b] Average pore diameter calculated from equation of Emmett and DeWitt,[16] equations (10) and (11) in text. [c] Ref. 13. [d] Ref. 15. [e] These isotherms are of Type IV, but without hysteresis.

assuming the values of surface area from $S(1 + j)/2$ and the free energies from equation (9) to be correct. These computed surface free energies given in the last column of Table II are usually always larger than the normal surface tension, in some cases being nearly twice as large. The data for the isotherms of *n*-butane are computed for both of the surface areas given in Table I.

Application of Equation (4) to Type I Isotherms.—Equation (4) is useful in characterizing Type I isotherms[4] as shown in Figs. 5 and 6 for silica gels and charcoals. The data for these and similar isotherms are given in Table III. Lambert's isotherms of benzene on silica gel are definitely of Type I, while the ethanol isotherms as shown in Fig. 5 appear similar to those of some iron gels. Although the values of j and k vary considerably, the surface areas calculated from benzene and ethanol isotherms are nearly identical. Recently, Emmett and Anderson[15] presented isotherms showing the effect of high temperature evacuation on charcoals. In charcoal PCI-1042 (Fig. 6) the evacuation caused sintering and enlargement of pores indicated by a decrease in V_m and an increase in the value of j, as shown in Table III. With charcoal NS_5 less sintering and relatively less pore size alteration occurred as indicated by the changes in V_m and j.

Relation of j to Average Pore Diameter.—Emmett and DeWitt[16] presented a useful method of estimating the average pore diameter, based on cylindrical pores

$$\bar{d} = 4V_L/A \qquad (10)$$

where V_L is the volume of adsorbate necessary to fill pores computed as normal liquid and A the surface area. Introducing equation (3) into equation (10)

$$\bar{d} = 6.56 \frac{M}{\rho a} \frac{1}{1 - j} \qquad (11)$$

where d is the average pore diameter in Å., M and ρ the molecular weight and density of adsorbate, respectively, and a the cross-sectional area of the adsorbate molecule in sq. Å.

Equation (11) has been used to compute average pore diameters from the isotherms of Tables I and III. The average pore diameters from the nitrogen and argon isotherms agreed quite satisfactorily, but the diameters from the butane isotherms were considerably larger. It has been pointed out in the literature that the cross-sectional area of molecules as computed by the method of B.E.T.[3] may not be correct, especially with long molecules like *n*-butane. If the cross-sectional area of butane is taken 1.75 (the average of the ratios of the areas from nitrogen and argon to areas from butane, computed by the usual B.E.T. methods) times the value of 32.1 Å.,[2] the average pore diameters computed from isotherms of the three gases are in fairly good agreement as shown in Table I. For pores that are the order of several molecular diameters, equation (11) does not hold, the diameter calculated being larger than the actual diameter. For the limiting case when the only one molecule fits into the capillary, $\bar{d} = 4V_L/\pi A$. For values of j less than 0.16 (the value of j for a pore of 3 molecular diameters), the constant in equation (11) should be less than 6.56 and greater than 2.09. Since in equation (9) $\bar{d} = \Sigma d^2/\Sigma d$, this average pore diameter will be larger than the arithmetic mean if there is a wide distribution of pore diameters; therefore, any diameter computed by equations (10) and (11) may be regarded as an upper limit of the pore diameter.

Discussion

Constant k of equation (4) is an average value of the k's for all of the adsorbed layers in the capillary system. Since d in the expression $k = \exp d/RT$ is equal to the change in surface area times the surface free energy, the values of k for a given pore system should be greater in higher layers than in those near the surface. Similarly for the same adsorbate on different adsorbents k should be nearly equal to 1 for large pores and

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(15) Emmett and Anderson, *J. Phys. Colloid Chem.*, **51**, 1308 (1947).

(16) Emmett and DeWitt, THIS JOURNAL, **65**, 1253 (1943).

have higher values for small pores. Should the adsorbent offer considerable convex surface to adsorption in the first several layers, the value of k may be expected to be less than 1. This is shown in the data of Table I. It is difficult to explain the values of $k = 1$ observed for isotherms approaching Type I. There is no objection to $k = 1$ for isotherms that are strictly of Type I in which all of the adsorption occurs in the first layer. However, for the isotherms of the two PCI-1042 charcoals the values of k might be expected to be considerably larger than 1, since the isotherms indicate multilayer adsorption and since the average pore diameters are smaller than those of the Type IV isotherms of Table I. It is possible that these charcoals are composed of small pores plus a fraction of larger pores that cause the adsorption at higher relative pressures. In this case equation (4) may be regarded as somewhat empirical; however, V_m from this equation and the values of j probably have their usual significance.

With most isotherms the simple B.E.T. equation usually predicts larger adsorption above relative pressures of 0.35 than the actual isotherm, and deviation in this direction is usually considered to occur with all isotherms. It is interesting to note that the isotherms in Table I for which jk is greater than 1 deviate from the simple B.E.T. equation in the opposite direction.

In a previous section adsorption was postulated to occur in the same manner as multilayer adsorption with the decreased free energy of adsorption due to capillary forces causing the pores to fill at a lower relative pressure than 1. Equation (4) was found to satisfactorily fit the data for the adsorption branch of the isotherms, but could not be fitted to the desorption branch. This may indicate that desorption occurs in a different manner. In the authors' opinion desorption occurs from menisci of filled pores to leave the pores covered with the number of layers predicted by equation (4) remaining on the surface. This is similar to the picture of adsorption and desorption given by Cohan[17] except that he postulated that the pore will empty completely on capillary evaporation.

Equation (4) provides a systematic method of determining V_m for isotherms to which the simple B.E.T. equation cannot be fitted. This is also true of isotherms which appear to be a composite of several types of simple isotherms such as those of the porous carbon blacks previously described,[8] and some of the isotherms of active magnesia of Zettlemoyer and Walker.[18] In the latter case equation (4) can be applied satisfactorily to relative pressures of 0.4 by taking jk greater than 1.

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Summary

1. A modified B.E.T. equation similar to that of Anderson[8] has been derived and applied to physical adsorption isotherms of Types I and IV.[4]

2. With Type I isotherms satisfactory fit of this equation can be obtained if the free energy of adsorption in the second and subsequent layers is taken to be equal to the heat of liquefaction.

3. For isotherms of Type IV which flatten below relative pressures of 0.85, the equation satisfactorily fits the data, if the free energy of adsorption was taken less than that of liquefaction. For this kind of Type IV isotherm the equation was used to integrate the equation of Kistler,[9] and the resulting expression gave surface areas of the same order of magnitude as the B.E.T. areas.

4. The equation is believed to be a simple method of characterizing isotherms with four constants.

[17] Cohan, *ibid.*, **66**, 98 (1944).

[18] Zettlemoyer and Walker, *Ind. Eng. Chem.*, **39**, 69 (1947).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

The Sorption of Gases on a Plane Surface of Two Stainless Iron–Chromium–Nickel Alloys at 20, −78 and −183°[1]

BY MARION H. ARMBRUSTER

The resistance to corrosion and other properties of the stainless iron alloy containing approximately 18% chromium and 8% nickel suggest that the surface of the alloy may differ considerably from that of ordinary steels. As it seemed likely that the sorption of gases on such an alloy might yield a clue to the character of the surface and, by comparison with data for steels, might indicate differences in the nature of the surface, the sorption of hydrogen, neon, argon, nitrogen, carbon monoxide and oxygen has been measured at 20, −78 and −183° and at pressures up to 0.1 cm. mercury. The sorption of carbon dioxide has been determined at −78 and −183°.

The apparatus used, its calibration and method of operation have previously been described.[2] The gases were likewise those used in an earlier study of sorption on mild carbon steel.[3]

[1] Presented in part before the Chemical Research Conference on Catalysis sponsored by the American Association for the Advancement of Science, at New London, N. H., June 23–28, 1947.

[2] Armbruster and Austin, THIS JOURNAL, **60**, 467 (1938); **61**, 1117 (1939).

[3] Armbruster and Austin, *ibid.*, **66**, 159 (1944).