The Molecular Cross-sectional Areas for the Determination of Specific Surface Areas of Solids. I. Carbon Black

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Various methods have been developed to estimate the specific surface areas of solids from the theory of physical adsorption. Among them, most widely used is the Brunauer-Emmett-Teller, or B. E. T. method(1). In this method, the number of adsorbed molecules necessary to cover the surface of 1 g. of a solid completely with a monomolecular layer is evaluated by so-called B. E. T. equation, i. e.,

$$\frac{P}{V(P_s-P)}=\frac{1}{V_mC}+\frac{(C-1)}{V_mC}\cdot\frac{P}{P_s} \qquad (1)$$

where P is the equilibrium pressure, P_s the saturation pressure of the adsorbate gas, V the volume of the gas adsorbed at S. T. P., V_m that necessary to cover the surface with a monomolecular layer, and C a constant.

Specific surface area is then obtained by multiplying V_m with the molecular cross-sectional area, σ, which is given by the following equation:

$$\sigma = 1.091(M/N\rho)^{2/3} \qquad (2)$$

where M is the molecular weight, ρ the density in the liquid (or solid) state of the adsorbate, and N Avogadro number. If the number of molecules in a monomolecular layer and the cross-section obtained above were correct, the calculation would give an absolute surface area, and the values obtained by different adsorbates should agree. But it is well known, generally, that this is not the case. For instance, Jacobs and Tompkins(2) stated that most adsorbates yield surface areas that require multiplication by a factor of between 1.2 and 1.5, and in extreme cases 2 or 3, to give areas agreeing with those calculated from the nitrogen isotherms. This disagreement may arise from either of two reasons: (1) the B. E. T. equation cannot be applied satisfactorily for the isotherms; and (2) equation 2 for σ fails to give a correct cross-section of an adsorbate molecule on the surface. Existence of chemisorption, active spots, and pores or cracks on the surface mainly affects the type of isotherm while packing of adsorbate molecules on the surface affects σ because the factor 1.091 in equation 2 is calculated from the assumption that the adsorbate molecules on the surface is spherical closest packing, i. e., three dimensionally 12 co-ordination and two dimensionally 6 co-ordination. Therefore, it is very difficult to know the absolute value of the surface area by this method. Thus, to compare surface areas using different gases, relative values of cross-sections should be determined beforehand.

On the other hand, Harkins and Jura(3) have developed the absolute calorimetric method to measure the absolute surface area without the knowledge of the cross-section of the adsorbate molecule. But this method has not been employed generally, because it can not be applied to solids which have pores and cracks and the method of measurement is so difficult that its applicability is rather limited.

Livingston(4) examined published data about the measurements of the specific surface areas of oxides by the B. E. T. method and assigned the cross-sections of adsorbate molecules which might give the consistent areas for oxides. He took the case of adsorption of nitrogen at −195° as a standard process and assigned the value 15.4 Å^2 for the cross-section of a nitrogen molecule instead of widely used value, 16.2 Å^2, obtained from equation 2 using liquid density of nitrogen. Cross-sections of the other gas molecules were, then, determined so as to give equal surface area with nitrogen. These values are shown in Table V, column 5. These values, however, can not necessarily give consistent surface areas for other solids than oxides. In the experiments described below, adsorption of several gases on carbon black samples was measured by the same

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1) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 301 (1938).

2) P. W. M. Jacobs and F. C. Tompkins, "Chemistry of the Solid State", edited by W. E. Garner, Butterworth Scientific Publications, London (1955), p. 91.

3) W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 1362 (1944).

4) H. K. Livingston, *J. Colloid Sci.*, **4**, 447 (1949).

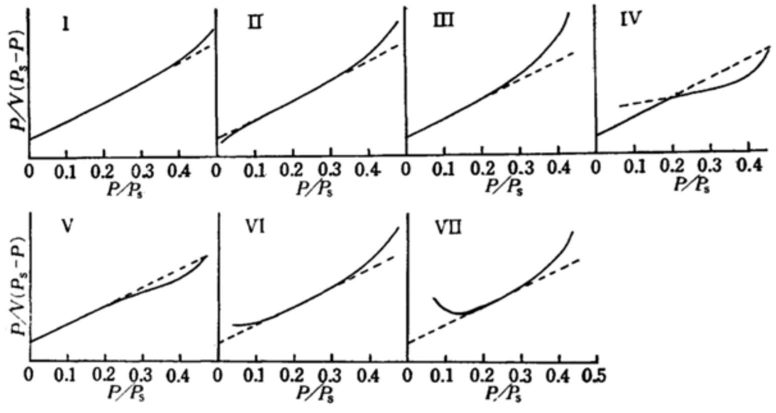

Fig. 1. Types of B. E. T. curves.

apparatus under similar experimental conditions. The specific surface areas of the adsorbents were then calculated and by comparing them with each other and with the values obtained from the electron microscopy, and taking into consideration of the two dimensional van der Waals' constant of argon, the molecular cross-section for each adsorbate gas which would give consistent surface area was determined. Gases were also examined to discover whether they were suitable for this purpose or not.

Experimental Method and Results

A series of 8 commercial carbon blacks listed in column 2, Table I, were used in this experiment. Nitrogen, argon, oxygen, carbon dioxide and *n*-butane were chosen as adsorbate gases.

The apparatus for the adsorption measurement was an ordinary volumetrical type. Temperatures of the adsorbents were measured by a vapor-pressure thermometer with suitable vapors. Samples of carbon black were heated at 200°C in the apparatus and evacuated until pressure in the apparatus reached 1×10^{-5} mmHg every time before the adsorption was measured. In most cases adsorption isotherms were taken between the relative pressures of 0.02 to 0.35, and in some cases up to 0.90. Measured values of $P/V(P_s-P)$ were plotted as a function of P/P_s, according to equation 1. Curves obtained were classified in 7 types as shown in Fig. 1.

Curves I and III have similar forms, but the former has a longer linear portion which extends over 0.35 of P/P_s. Curve II is the most general form which has the linear part from 0.05 to 0.2 or more, and below 0.5 deflects downwards. Curves IV to VII are of special types which appear in a few cases.

In Table I, types of curves obtained are listed together with the appearance of the hysteresis in the measured pressure range.

V_m was calculated from the linear parts of these curves and shown in Table II. From these values of V_m, specific surface areas of the adsorbent were calculated using molecular cross-sections in column 4, Table V, which were calculated by equation 2 using the liquid density of each gas at measured temperatures⁵⁾. The values are shown in Table III. The ratio S_{N_2}/S is that between surface area measured by nitrogen and that of the other gas. Surface areas measured by the absolute method by Okuda and Tanaka⁶⁾ and from electron microscopy by Suito and Arakawa⁷⁾ are shown for comparison. It should be remembered that the latter values were calculated from average particle diameter $d_1=\sum nd/\sum n$, assuming the density of carbon black to be 1.8, whereas values from the adsorption correspond to $S=K(\sum nd^2/\sum nd^3)$, where K is a shape factor.

Discussion

As are shown in Table III, the ratios of surface area by nitrogen adsorption to that by argon adsorption (S_{N_2}/S), for both adsorption temperatures are 1.14 and their standard deviations are small. For oxygen and *n*-butane, the standard deviations in area ratios are greater and for carbon dioxide the greatest, even with the exclusion of No. 6.

Applicability of the B.E.T. isotherm can be judged from the range of the linear part on the curve. From Fig. 1 and Table I, it is seen that argon (−183°C) and oxygen show largest range of linear part and then follow nitrogen and argon (−196°C). Of

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5) P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 1153 (1937).

6) S. Okuda and N. Tanaka. The report to be published soon in *J. Ceramic Association, Japan.* (*Yogyo Kyokai Shi*).

7) E. Suito and M. Arakawa, "Collaborative Research Reports of the Ministry of Education." (Chemistry), p. 120 (1956). Data given by the authors were average particle diameter d_1, from which the surface areas shown in the table were calculated.

TABLE I
TYPES OF B. E. T. CURVES

No.	Black	$N_2(-196°C)$		$Ar(-196°C)$		$Ar(-183°C)$		$O_2(-183°C)$		$CO_2(-78°C)$		$n\text{-}C_4H_{10}(0°C)$	
		Type	Hyst.	Type	Hyst.	Type	Hyst.	Type	Hyst.	Type	Hyst.	Type	Hyst
1	Peerless II A	III	−	III	−	III	−	III	−	III	−	III	+
2	Philblack-E	I	−	I	−	I	−	I	−	II	+	I	−
3	Tokai S. 285	III	−	III	−	II	−	I	−	II	+	I	+
4	Denka 2000	III	−	III	−	I	−	I	−	II	−	I	−
5	Mi-ike 20	II	−	I	−	I	−	II	−	II	−	IV	+
6	P-33	III	−	I	−	I	−	II	−	II	−	II	+
7	Denka granular	IV	−	V	−	II	−	II	−	VII	−	II	+
8	Witoco	III	−	III	−	I	−	II	−	II	−	II	+

TABLE II
VALUES OF V_m

No.	N_2 cc./g.	$Ar(-196°C)$ cc./g.	$Ar(-183°C)$ cc./g.	O_2 cc./g.	CO_2 cc./g.	$n\text{-}C_4H_{10}$ cc./g.
1	80.7	85.4	80.3	89.6	58.5	27.5
2	30.6	30.6	29.5	32.4	19.6	11.3
3	21.1	22.0	21.2	23.8	14.5	7.58
4	9.93	10.1	9.76	10.0	6.21	3.83
5	3.97	4.15	3.88	3.88	2.69	1.51
6	3.67	3.66	3.62	3.53	1.12	1.38
7	14.6	16.0	14.7	15.2	10.3	5.98
8	27.1	27.1	26.2	33.1	20.8	9.23

TABLE III
SPECIFIC SURFACE AREAS MEASURED BY VARIOUS GASES

No.	$N_2(-196°C)$	$Ar(-196°C)$		$Ar(-183°C)$		$O_2(-183°C)$		$CO_2(-78°C)$		$n\text{-}C_4H_{10}(0°C)$		Electron micro-scope	Absolute method
	S_{N_2} $m^2/g.$	S $m^2/g.$	S_{N_2}/S	S $m^2/g.$	S_{N_2}/S	S $m^2/g.$	S_{N_2}/S	S $m^2/g.$	S_{N_2}/S	S $m^2/g.$	S_{N_2}/S		
1	351.5	317.3	1.11	311.0	1.13	340.0	1.03	267.7	1.31	237.0	1.48	99.0	
2	133.0	113.4	1.17	114.2	1.16	123.0	1.08	89.7	1.47	97.2	1.38	112.2	
3	91.9	81.6	1.13	81.9	1.12	90.3	1.02	66.4	1.38	65.4	1.41	60.6	46.4
4	43.2	37.6	1.15	37.8	1.14	37.9	1.14	28.4	1.52	33.0	1.31	81.3	
5	17.4	15.4	1.13	15.0	1.16	14.7	1.18	12.3	1.41	13.0	1.34	17.9	
6	16.0	13.6	1.18	14.0	1.14	13.4	1.19	5.1	(3.14)	11.9	1.35	22.8	
7	63.6	59.2	1.08	57.0	1.12	57.6	1.10	47.0	1.35	51.6	1.23	49.2	
8	118.0	100.5	1.17	101.4	1.16	125.5	0.94	95.3	1.34	79.6	1.48	91.6	109
Avarage			1.14		1.14		1.09		1.38		1.37		
Standard deviation			0.03		0.02		0.08		0.09		0.08		

The value in parentheses is excluded from the average.

TABLE IV
COMPARISON OF SURFACE AREA FROM B. E. T. METHOD AND ELECTRON MICROSCOPY

No.	N_2	$Ar(-196°C)$	$Ar(-183°C)$	O_2	CO_2	$n\text{-}C_4H_{10}$
1	(3.54)	(3.20)	(3.14)	(3.44)	(2.10)	(2.40)
2	1.18	1.01	1.02	1.10	0.80	0.87
3	1.52	1.35	1.35	1.49	1.10	1.08
4	(0.53)	(0.46)	(0.46)	(0.47)	0.35	(0.41)
5	0.97	0.86	0.84	0.82	0.69	0.73
6	0.70	0.60	0.61	0.59	(0.22)	0.52
7	1.29	1.20	1.16	1.17	0.96	1.05
8	1.29	1.10	1.11	1.37	1.04	0.87
Average	1.16	1.02	1.02	1.09	0.823	0.853
Mol. cross-section	14.0	13.5	14.2	12.9	20.7	37.6 Å^2

these two, argon (−196°C) has longer linear portions though not listed in the table. By *n*-butane, linear parts are also large but in most cases isotherms show hysteresis. Carbon dioxide is inferior to the other gases. Among the adsorbents used, No. 7 exhibits anomalous isotherms for all gases.

From the above facts, nitrogen and argon turned out to be the most suitable adsorbates for the surface area measurement of carbon black, while oxygen and *n*-butane are seen to be somewhat inferior to the former two. Carbon dioxide is not suitable for this purpose. From the surface ratio values in Table III, except for No. 6 by carbon dioxide, it is possible to eliminate the differences in surface areas measured by different gases by assigning a proper molecular cross-section for each gas. In doing this, a gas which might be considered to give the specific surface area nearest to the absolute surface should be chosen as a standard gas; then, the cross-section of other gases could be determined to give the equal surface area as the standard gas. Generally, nitrogen is used for the B. E. T. method with the cross-section of 16.2 Å², but it generally gives a larger surface area when compared with that by the other gases and also with the value obtained by electron microscopy or the absolute method. To compare surface area values by the B. E. T. method with those by electron microscopy, ratio of the values by the two methods was calculated for each carbon black with various gases and listed in Table IV*. It is seen from the table that the agreement of values between the two methods is best for argon, whereas nitrogen adsorption gives somewhat greater values. The molecular cross-section of each gas used for the evaluation of the surface area was divided by the respective average ratio and shown in the bottom of the table. These are cross-sections which will give surface areas in agreement with those from electron microscopy. For carbon black, Anderson and Emmett[8] concluded that 16.2 Å² is better than 13.8 Å² calculated from the solid density. On the other hand, Arnell and Henneberry[9] compared the surface areas of carbon blacks measured by permeability, electron microscopy, and the B. E. T. method using nitrogen cross-section of 16.2Å². The results revealed that the surface areas measured by the B. E. T. method was 30% larger in average than those by the other methods (except for samples which had pores and cracks as mentioned by Arnell et al.).

From the above considerations, the value 16.2 Å² for nitrogen cross-section would be too large. The concept of two dimensional gas of adsorbed molecules suggests that the molecular cross-section should be nearly equal to the two-dimensional van der Waals' constant[10]. For nitrogen this value is 15.4 Å²; Livingston used this value as a standard and estimated the cross-section of other gases from this value. In the above experiment both nitrogen and argon proved to be suitable for this method, but from Table IV, it is seen that argon gives surface areas more consistent with those by electron microscopy than nitrogen does. In addition, the following facts point to the superiority of argon to nitrogen, i. e., in the plot of equation 1, generally, the former has longer linear part than the latter. Moreover, argon shows no chemisorption and exhibits more ideal packing state on the surface as it consists of monoatomic molecules and has no quadruple moment which nitrogen has to some extent[11]. The fact that the agreement between the two dimensional van der Waals' constant and the value from the equation 2 is better in argon than in nitrogen, seems to show that the former exhibits more ideal packing state on the surface than the latter does. Therefore, argon was taken as a standard. For the molecular cross-section of argon, three values were obtained, i. e., 13.5 Å² from comparison with electron microscopy, 13.8 Å² from equation 2 using liquid density at −195°C, and 13.6 Å² from the van der Waals' constant. Among these three values, 13.8 Å² from equation 2 was employed as a standard, because the differences among these values are rather small and there is no serious reason to change the generally employed value from equation 2. The molecular cross-section thus determined, those given by Livingston,

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* Values in parentheses are the largest and the smallest ratios for each gas and are excluded from the average, because corresponding samples might have some undesirable surface states or particle size distributions for this comparison.

[8] R. B. Anderson and P. H. Emmett, *J. Applied Phys.*, **19**, 367 (1948).

[9] J. C. Arnell and G. O. Henneberry, *Canadian J. Res.*, A, **26**, 29 (1948).

[10] J. H. de Boer, "Dynamical Character of Adsorption", Oxford (1953), p. 172.

[11] W. V. Smith and R. Howard, *Phys. Rev.*, **77**, 132 (1950).

TABLE V

MOLECULAR CROSS-SECTIONAL AREAS

Gas	Temp.	van der Waals' const.	Eq. 2 Liq. state.	Livingston's	Present Authors'
N_2	−196°C	15.4 Å^2	16.2 Å^2	15.4 Å^2	14.2 Å^2
Ar	−196	13.6	13.8	14.6	13.8
Ar	−183	13.6	14.4	15.5	14.4
O_2	−183	13.5	14.1	14.6	13.5
CO_2	− 78	16.5	17.0	19.5	20.8
n-C_4H_{10}	0	33.0	32.1	44.6	38.6

TABLE VI

SPECIFIC SURFACE AREAS

No.	N_2 S m^2/g.	Ar(−196°C) S m^2/g.	Ar(−183°C) S m^2/g.	O_2 S m^2/g.	CO_2 S m^2/g.	n-C_4H_{10} S m^2/g.	Elec. micro.	Abs. method
1	304.0	317.3	311.0	325.0	327.0	285.0	99.0	
2	116.7	113.4	114.2	117.7	109.6	116.7	112.2	
3	80.5	81.6	81.9	86.3	81.1	78.8	60.6	46.4
4	37.9	37.6	37.8	36.3	34.7	39.7	81.3	
5	15.3	15.4	15.0	14.1	15.0	15.6	17.9	
6	14.0	13.6	14.0	12.8	6.2	14.3	22.8	
7	55.8	59.2	57.0	55.1	57.5	62.1	49.2	
8	103.5	100.5	101.4	120.0	116.6	95.8	91.6	109

ordinary values from equation 2 and the two dimensional van der Waals' constants are shown in Table V. It is seen that the values agree surprisingly well with those in Table IV except oxygen. The value for oxygen agrees with that of van der Waals' constant. The value for nitrogen becomes smaller than that from equation 2 and of Livingston. Livingston said that according to the results of Arnell and Henneberry for 9 carbon blacks, nitrogen adsorption surfaces are about 12% higher than the values by permeability and electron microscopy. It is not clear how Livingston estimated the value of 12%, but if nitrogen cross-section 16.2 Å^2 used by Arnell and Henneberry is reduced by 12%, it gives 14.5 Å^2 which nearly agrees with the present value.

The specific surface areas calculated by these cross-sections are listed in Table VI. Comparison with the values by the absolute method shows good agreement in case of No. 8, while in No. 3, the absolute method gives a far smaller value. The electron microscopy also gives a smaller value for the latter sample. If there were small pores and cracks on the surface of the latter, unobservable by the electron microscope, these would be covered by the adsorbate in the case of the absolute method, so that both methods might give lower values than the B. E. T. method does. Other small values by electron microscopy are also explainable by the existence of pores and cracks. Thus, Nos. 1, 3 and 8 show somewhat lower values also by n-butane adsorption which suggest the existence of small pores, into which rather large n-butane molecules can not penetrate.

In electron microscopy, as is described above, the surface areas were calculated from $d_1 = \sum nd/\sum n$, assuming all the particles to be spherical. Calculation from d_1 gives correct surface area only when all the particles have the same size. Generally, this is not the case, and owing to the particle size distribution, this calculation gives too large a surface area. Moreover, as was pointed out by Arnell and Henneberry, if a small number of large particles were overlooked in measuring particle size by the electron microscope, surface area estimated from the results would give also higher value. Therefore, larger values than those by the B. E. T. method are not unexplainable.

No. 6 shows a remarkably small surface for carbon dioxide. The surface area of this sample for carbon dioxide increased as the temperature of heating before the adsorption rose above 200°C, although it remained constant for nitrogen and argon. This effect of heating temperature was seen only in this sample. This might be explained as the heat treatment above 200°C changed surface state of this sample, and also changed the state of adsorption of carbon dioxide molecules, but the adsorption of nitrogen and argon, which should be purely physical, would not be affected.

Conclusions

For the measurement of the specific surface areas of solid adsorbents, argon and nitrogen are most suitable for adsorbate gases. Oxygen and *n*-butane are also applicable but carbon dioxide may give unreliable results in some cases. The cross-sectional areas of adsorbed molecules listed in Table V, column 6, were determined to give consistent surface areas for different gases. The anomaly for carbon dioxide may be explained by the surface state of the carbon black.

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