Precise Evaluation of Surface Area With Indirectly Calculated Dead Space

William V. Loebenstein

The determination of surface area from nitrogen adsorption data obtained at low temperature by volumetric methods is subject to several errors. One error that becomes especially serious when the surface area is small is associated with the calibration of the dead space with helium. This error is large because the volume of adsorbed gas is calculated as a small difference between two comparatively large quantities.

A statistical method of successive approximations has been developed for calculating the dead space. The latter is obtained as that quantity necessary to yield the best agreement with the known isotherm equation. This procedure fixes the value of V_m (directly proportional to the surface area). The procedure also provides an estimate of the experimental error associated with the over-all determination.

1. Introduction

Adsorption of vapors at temperatures near their boiling points provides the most convenient means for determination of the surface areas of finely divided or porous solids. In volumetric apparatus, which is most commonly used, the amount of adsorbed gas is the difference between that admitted to the sample container and that remaining in the dead space. The latter is the void space between or within the solid particles plus the volume of the connecting tubing.

The precision with which a dead space calibration is normally made using helium is fairly well limited by the equipment and does not depend upon the surface area of the sample. The effect of this limitation of precision upon the measurement of the volume of gas (nitrogen, for example) adsorbed is especially serious when the surface area is relatively small. This is because the amount of gas adsorbed is calculated as the small difference between two large quantities. Indeed, the uncertainty in the measurement resulting from the dead space calibration is greater than that of all other factors which contribute to the over-all error of the surface area determination. It is difficult to express this fact using rigorous mathematical language because the surface area evaluation results from the parameters of a least-square line assumed to represent all of the points. No simple relationship exists between the over-all error and the errors associated with the determination of the individual points, especially since an error in the dead space actually destroys the linearity of the plotted curve.

Anyone who has made surface area determinations in the conventional manner can calculate from his own data the percentage change in surface area resulting from an error of, say, one percent in the dead space. The author has found that this error exceeded 100 percent for a sample of glass beads whose area was of the order of 0.2 m²/g as measured with N_2 at 90° K. Normally, of course, the careful technician would in such a case make sufficient replicate determinations of the dead space to insure that its precision was appreciably better than one percent.

In routine determinations where the isotherm equation is known from previous experience, the dead space need not be experimentally obtained. The surface area can be found by assigning a value for the dead space that will allow the experimental measurements to fit the known isotherm. This paper describes a procedure of successive approximations by which this is accomplished. The conservative technician may always prefer to determine the helium calibration directly. He can use the resultant dead space value as a starting point which may then be "refined" according to the technique described here. It is unnecessary to continue the refinement beyond the point in the calculations where the error of the dead space ceases to be the dominant factor contributing to the over-all error of the surface area determination.

It is fortunate that the adsorption isotherms which apply to a large number of materials measured at or near the boiling point of the adsorbate are expressible in one linear form or another. These are represented by the well known "Free Surface" equation of Brunauer, Emmett, and Teller [1][1] (BET) (eq 1), and by the equally familiar Langmuir equation (eq 2).

$$p/[V(p_0-p)]=[(C-1)/(V_mC)]\ p/p_0+1/(V_mC) \quad (1)$$

$$p/V=p_0/(V_mB)+p/V_m, \quad (2)$$

$p=$pressure attained when adsorption and desorption processes are at equilibrium,

$p_0=$vapor pressure,

$V=$volume of gas adsorbed STP,

$B, C=$constants (under conditions of the experiment) related to the energy of adsorption, and

$V_m=$a constant equal to the volume of gas (STP) required to cover the surface to the extent of one molecular layer.

---

[1] Figures in brackets indicate the literature references at the end of this paper.

2. Determination of the Dead Space Factor Z

The volume of adsorbed gas may be calculated from measurements as follows:

$$V = k \left[N - (fp/R)\, Z \right] \tag{3}$$

where N is the total number of moles of gas admitted to the adsorption tube and the quantity $(fp/R)Z$ represents the moles which remain in the gaseous state in equilibrium with the adsorbed phase. The factor f corrects for the nonideal behavior of a real gas at low temperatures. It is usually expressed as $(1+\alpha p)$ where α is a constant [2] depending upon the particular gas and its temperature. The quantity R is the gas constant in appropriate units; Z is the ratio of the dead space volume to the absolute temperature; and the proportionality constant k converts the moles of gas adsorbed to milliliters per gram at STP. The problem then is to choose a value of Z by trial so that with the measured values of N and p the best fit to the known isotherm equation is obtained.

It is customary in using the BET isotherm equation to plot $p/[V(p_o - p]$ as Y against p/p_o as X. The resulting graph is linear and may be written as follows:

$$Y = a + bX \tag{4}$$

where the intercept a and the slope b depend only on C and V_m. It should be noted that $1/V_m = a + b$. The surface area is determined by multiplying V_m by a packing factor characteristic of the gas adsorbed and of the temperature at which the isotherm was carried out.

The best value of Z in eq (3) is obtained when the resulting values for the gas adsorbed obey eq (4). It is not possible to determine Z with sufficient precision by graphical means alone, hence an analytical method was developed. This was achieved by considering eq (4) as a special case of the more general empirical equation

$$Y = a + bX + cX^2 \tag{5}$$

The least square value for the added parameter c can be determined and the value assumed for Z adjusted to make this coefficient approach zero.

The least square solution [2] for the coefficient c is

$$c = \frac{Sx^2 Sx^2 y - Sx^3 Sxy}{Sx^2 Sx^4 - (Sx^3)^2} \tag{6}$$

The denominator of eq (6) contains only terms [3] in x and, hence, is independent of Z and need not be determined. The numerator is designated by $F_{(Z)}$

$$F_{(Z)} = Sx^2 Sx^2 y - Sx^3 Sxy \tag{7}$$

As each successive choice of Z is made, the value of Y is computed for each experimental point and $F_{(Z)}$ evaluated from eq (7). If the new $F_{(Z)}$ is nearer zero than the last, the new choice has then resulted in an improvement in linearity.[4]

The question may arise as to how far this procedure need be carried before the results can be considered acceptable. This can be answered in terms of the experimental error as measured by the random scatter of the points. This is discussed in the next section of this paper. A standard deviation $s_{(1/V_m)}$ attributable to random scatter is relatively insensitive to small changes in Z. On the other hand, the value of $1/V_m$ may be extremely sensitive to changes in Z. Consider, therefore, two values of Z that produce corresponding values of $F_{(Z)}$, both greater than and less than zero, respectively. Two sets of values for Y may be determined and from these, two values of $1/V_m$. If the difference between these latter two is small compared with $s_{(1/V_m)}$, estimated from either set, no further improvement in Z can be justified by the data.

3. Estimate of Experimental Error

The preceding section was concerned with the contribution of the error of the dead space to the over-all variability of the results. When this is sufficiently reduced, the variability that remains is a measure of the scatter of the experimental points.

The errors associated with the regression parameters a and b may be readily calculated. Furthermore, an equation may be derived [3, 4, 5] for the standard deviation of the sum of a and b. The result may be written

$$s^2_{(1/Vm)} = s^2_{y \cdot x} [1/n + (1 - \overline{X})^2 / Sx^2]. \tag{8}$$

The term $s^2_{y \cdot x}$ is evaluated as follows [5, 6]

$$(n-3) s^2_{y \cdot x} = Sy^2 - (Sxy)^2 / Sx^2 \tag{9}$$

Confidence limits in $1/V_m$ may be determined by inserting "student-t" values into the relationship

$$\pm l(1/V_m) = [s_{(1/V_m)}] \, [t_{(n-3)}]. \tag{10}$$

---

[2] The following nomenclature is used throughout this paper:

X, Y are the individual points.
$n =$ number of points,
$\overline{X} = (\Sigma X)/n; \ \overline{Y} = (\Sigma Y)/n,$
$x = X - \overline{X}; \ y = Y - \overline{Y},$
$Sx^2 = \Sigma X^2 - (\Sigma X)^2/n,$
$Sy^2 = \Sigma Y^2 - (\Sigma Y)^2/n,$
$Sxy = \Sigma XY - (\Sigma X)(\Sigma Y)/n$
$Sx^3 = \Sigma X \cdot X^2 - (\Sigma X)(\Sigma X^2)/n$
$Sx^2 y = \Sigma X^2 Y - (\Sigma X^2)(\Sigma Y)/n,$ and
$Sx^4 = \Sigma X^2 \cdot X^2 - (\Sigma X^2)^2/n$

[3] Pressure (or relative pressure), which is taken as the independent variable, is assumed to be measured without error. While this is not strictly true, the assumption is permissible since these errors are probably very small as compared with those for derived quantities such as the volume of gas adsorbed, which appears in the ordinate. Furthermore, the errors in Y are assumed to be completely random and normally distributed about a mean of zero.

[4] The quantity $F_{(Z)}$ (as it passes through zero) has a positive slope (with respect to Z). An estimate of the magnitude of this slope from previous choices aids in the selection of Z.

[5] The quantity $(n-3)$ is preferred here as a more conservative estimate of the number of degrees of freedom than $(n-2)$. This is because the data have been utilized for the determination of three parameters instead of the usual two.

[6] In computing $s_{y \cdot x}$ from eq (9), rounding off by dropping of digits should be postponed until the end of the operation, otherwise serious errors may be introduced.

Hence, the confidence interval surrounding V_m (which is proportional to the surface area) is given as

$$\frac{1}{1/V_m + l(1/V_m)} \lesssim V_m \lesssim \frac{1}{1/V_m - l(1/V_m)}. \quad (11)$$

The 95-percent confidence limits are implied if not otherwise stated. In layman's language this means that the interval determined by the stated limits will, on the average, bracket the correct value of $1/V_m$ 95 percent of the time. The appropriate "student-t" values may be found in any elementary textbook on statistical methods.

The method outlined will now be applied to a 24.4188 g sample of Pitch Coke (Koppers Co.) which was found to have a surface area of 1.6 m^2/g. Table 1 summarizes the adsorption measurements using nitrogen at 90° K for which the BET free-surface equation was known to apply. The values in the second column of table 1 were determined with use of eq (3) to express V in terms of Z. Values of some of the quantities used in this example are $k = 917.32$ ml/mole; $R = 6.236 \times 10^4$ (mm Hg) (ml) (mole)$^{-1}$ (°K)$^{-1}$ $f = 1 + 3.3 p \times 10^{-5}$; and 2,715 mm $\lesssim p_0 \lesssim$ 2,722 mm.

TABLE 1. *Adsorption measurements of N_2 at 90° K on Pitch Coke (Koppers Co.)*

Relative pressures (X)	$\dfrac{p}{V(p_0 - p)}$ [V expressed in terms of Z by eq (3)]
0.0969	(1.1700)/[9.367—(42.670)Z]
.1411	(1.7909)/[12.469—(62.366)Z]
.1765	(2.3364)/[14.942—(78.231)Z]
.1972	(2.6769)/[16.290—(87.508)Z]
.2182	(3.0430)/[17.893—(96.916)Z]
.2341	(3.3322)/[18.870—(104.080)Z]
.2540	(3.7118)/[20.375—(113.057)Z]
.2679	(3.9887)/[21.243—(119.425)Z]

The geometry of the adsorption vessel furnishes a means to estimate the first values to be ascribed to Z. After a few trials the choice of Z was narrowed down to within 0.135 and 0.137 for which $F_{(Z)}$ was less than zero and greater than zero, respectively. An estimate of the standard deviation was made according to eq (8) and the results are entered in table 2.

It can be seen from table 2 that the difference between the two values for $1/V_m$ for the first comparison amounts to more than three times the estimate of $s_{(1/V_m)}$. This means that further improvement in Z should be made in order that the limiting factor in the precision of the experiment be the random scatter of the points. It is significant that if the dead space had been calibrated directly, and the results obtained were 12.15 and 12.33 ml for duplicate determinations, the agreement would have been considered acceptable. Yet these values correspond to 0.135 and 0.137 for Z which has just been shown to have too wide a spread to be acceptable.

Upon further refinement of the computations by successive approximations, the spread in Z was decreased to fall within 0.1362 and 0.1363 and the results are also summarized in table 2. The difference between the values of $1/V_m$ has now been diminished to an acceptable value of 0.009 since this is only about one-fifth the standard deviation of $1/V_m$. Hence, there is no need for further refinement. The average of the acceptable values of $1/V_m$ is 2.786 with 95-percent confidence limits of ± 0.1267. This corresponds to a surface area of

$$1.656 \, {}^{+0.080}_{-0.072} \, m^2/g.$$

4. Application to the Langmuir Equation

The development is simpler in the event that the isotherm applicable to the data is the Langmuir equation (eq 2) where now $1/V_m = b$. The quantity p/v when plotted as a function of p results in a straight line providing the correct dead space is used. The experimental error is obtained by the same reasoning that was used in the previous section. Equation (9) is equally applicable for determining $s^2_{y \cdot x}$. However, instead of eq (8), the corresponding relationship is

$$s^2_{(1/V_m)} = s^2_{y \cdot x}/Sx^2. \quad (12)$$

The remainder of the treatment for this case is exactly the same as that already described.

5. Discussion

The effect of an error in the dead space upon the determination of the volume of gas adsorbed becomes especially serious whenever the amount of adsorbed gas is small compared with the unadsorbed gas. Indeed, the uncertainty in the measurement of the dead space can overshadow the unreliability of all other factors which contribute to the over-all error in V_m. This error can be decreased appreciably by a different choice of experimental conditions designed to increase the adsorption. The use of krypton as the adsorbate at liquid nitrogen temperatures has become increasingly popular in this connection especially where the surface areas to be measured are extremely small (i. e. of the order of 100 cm^2/g).

The technique described in this paper is not proposed as an alternative to the use of krypton, but rather as a supplement. It can be applied to isotherms obtained with krypton as well as with

TABLE 2. *Results of successive approximations*

	1st comparison			2d comparison		
Z	0.135	-----	0.137	0.1362	-----	0.1363
$F_{(Z)} \times 10^5$	−.022	-----	+.012	−.006	-----	+.002
$1/V_m$	2.686	-----	2.850	2.782	-----	2.791
$\Delta(1/V_m)$	-----	0.164	-----	-----	0.009	-----
$s_{(1/V_m)}$	0.047	-----	0.051	0.049	-----	0.049
$\pm l_{(1/V_m)}$	-----	-----	-----	-----	-----	.1269
			.1264			

nitrogen or any other gas for that matter, as long as the isotherm equations are applicable. For many practical reasons [7] it is desirable to use nitrogen in preference to krypton where at all possible. The limiting criterion should be whether sufficient precision is obtainable using nitrogen based upon the scatter of the adsorption points alone.

It is a common experience in many laboratories to repeat adsorption measurements because many of the points fail to conform to the BET isotherm equation. Small errors in the dead space could account for such failures, especially when the volume adsorbed is small. For such cases the technique of this paper is of considerable value.

There may be reasons for discrepancies existing between measurements of dead space and their correct values other than the usual limitations in the precision of the experimental observation. Helium may itself be adsorbed upon certain materials [8] at the temperature of the dead space calibration. Also, probably more commonly than realized, adsorbents may have an appreciable volume within pores larger than that of the helium molecule, but smaller than nitrogen. This would give rise to a molecular-sieve phenomenon that might alter the dead space obtained from a helium calibration.

The most reliable estimate of surface area is obtained by taking the arithmetical mean of several independent determinations. In this way, chance variations even among samples can be averaged out. Such a procedure for as few as two determinations can seldom be justified economically. The only practical alternative is to make a single determination. Hence, it is especially important to select a representative sample and to employ an analytical technique which leads to results of the highest precision that the data are capable of yielding. An estimate of this precision is also very desirable. It is believed that the present work accomplishes these ends.

Obviously, the calculations are somewhat more time consuming with the proposed technique than with the conventional method of determining dead space. The time saved by elimination of the dead space calibration partially compensates for the additional time required for the calculations.

The more experimental points taken within the applicable pressure range of the isotherm equation, the better one is able to distinguish between experimental error and incorrect dead space. However, a large number of points is time consuming, and increases the possibility of introducing errors due to undetected changes in experimental conditions. While it is beyond the scope of this paper to determine rigorously the minimum number of points required, it is felt from experience that about eight is a practical compromise.

The helium calibration employed in the conventional method for surface area determination sometimes poses a problem not universally encountered. The limited availability of helium in many areas could act as an effective deterrent for its use, particularly where surface area measurements are of a routine nature. For these localities a technique such as that described in this paper should be especially attractive.

6. References

[1] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[2] W. V. Loebenstein and V. R. Deitz, J. Research NBS **46**, 51 (1951) RP2174.
[3] W. E. Deming, Statistical adjustment of data, p. 167 (John Wiley & Sons, 1943).
[4] F. D. Rossini and W. E. Deming, J. Wash. Acad. Sci. **29**, 416 (1939).
[5] S. S. Wilks, Mathematical statistics, p. 158 (Princeton Univ. Press, 1943).

Washington, August 26, 1957.

---

[7] 1. Highly sensitive differential pressure measuring techniques are required since all the adsorption points must fall within the pressure range of 0.2 to 0.6 mm where the BET isotherm is valid.
2. Long periods of time are required before equilibrium is attained at each adsorption pressure.
3. Thermal transpiration (thermo-molecular diffusion) effects become so pronounced that special calibration is required to correct for this phenomenon.

[8] A polymer carbon described by F. H. Winslow, W. O. Baker, N. R. Pape, and W. Matreyek, J. Polymer Sci. **16**, 101 (1955) adsorbed 3 cm³ of helium per g even at 30° C. The surface area of this sample (nearly 600 m²/g) was determined from its nitrogen adsorption at 90° K. The absolute error of the dead space was quite large because of the appreciable adsorption of helium at that temperature. The relative effect of this error upon the surface area was neglibible, however, because of the very large adsorption of nitrogen as compared with the unadsorbed gas in equilibrium with it.