

Unbound Water Content From Application of Adsorption Theory

William V. Loebenstein

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

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It is standard procedure to fit an applicable isotherm equation to water vapor adsorption data using the method of least squares in arriving at a value for the surface area accessible to the water molecule. The least squares technique has been extended in the present investigation to determine, in addition and simultaneously, a "best value" for the zero-humidity sample weight of the material. The application is equally valid for desorption insofar as the zero-humidity weight is concerned, although the derived value for "surface area" from desorption data will be over-estimated in the general case because of hysteresis. There is no limitation on the range of humidities since the method is not restricted to the BET equation (i.e., between 0.1 and 0.3 r.h.). In fact, good agreement with the zero-humidity points measured experimentally has been obtained even from drying curves in which the relative humidity has been confined to the region above 50 percent. An iterative method is employed in the calculations for which computer assistance is especially adaptable. Fortran IV programs are included in the appendix whose use requires no extensive computer experience. A fraction of a second in computer processing time is all that is required for each determination.

Key words: Adsorption; computer application; desorption; dry weight determination; moisture content; surface area; water content; water vapor adsorption.

1. Introduction

What constitutes the dry weight of a solid has never been completely resolved. Some materials like hydroxide gels of aluminum, silicon, iron, etc., continue to lose water when evacuated at ambient temperatures and more so on heating, yet a trace of water always seems to remain. Other materials readily give up their water, but suffer irreversible changes in the process. This leads to the adoption of a concept of water of constitution as distinguished from excess water.

A novel approach to this problem of dry weight prediction is portrayed in this paper based on the assumption that adsorbed water is certainly not water of constitution, and, consequently, is excess. To establish the precise point of dryness, therefore, it is only necessary to determine the weight of the solid under conditions where the amount of physically adsorbed water would be zero. This is determined by fitting vapor adsorption theory to the experimental data by an unorthodox application of the least-squares technique.

Since the development in 1938 of the Brunauer, Emmett, and Teller (BET) multimolecular adsorption free-surface equation [1]¹, many other adsorption isotherm theories [2, 3, 4, 5, 6, 7] have appeared in the literature. Most of the resultant isotherm equations,

despite their differences, shared certain important attributes:

- (1) They were expressible in some linear form.
- (2) Each equation possessed physically significant parameters which could be evaluated either from the slope or intercept of the experimental plot or a combination of both.
- (3) These parameters bore a simple functional relationship with the specific surface of the adsorbent.

For these reasons, any such theory would appear to qualify as a candidate for prediction of dry weight in the method to be described.

At the onset of this study, no *a priori* preference was made of any one adsorption theory over the others, although, in practice, the BET equation is probably more widely used than all of the others combined. This reason alone would justify its inclusion among the theories selected. In addition to the BET, the other adsorption theories tested in this work were: the Polarization theory [6], Harkins and Jura (H-J) theory [3], and Polanyi's Potential theory [6].

It will be shown that the same experimental points that are normally employed using least-square methods to determine only the surface area of an adsorbent can, at the same time, be called upon to furnish an additional piece of information; namely, its dry weight.

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

2. Theoretical Development

(1) The BET [1] free-surface equation in its most familiar form may be represented as a linear function of the relative pressure:

$$y = a + bx \quad (1)$$

where x = relative pressure (humidity, where water vapor is the adsorbate) expressed as a dimensionless decimal such that $0 \leq x \leq 1$. The dependent variable y is, in itself, an expression:

$$y = x/[q(1-x)] \quad (2)$$

containing both x and q . The latter quantity represents the number of moles of adsorbate per g of adsorbent obtained under steady state conditions at the corresponding value of x .

The y -intercept, a , and slope, b , are the parameters $1/(q_m c)$ and $(c-1)/(q_m c)$, respectively. The quantity q_m , in turn, represents the number of moles of adsorbate required to constitute a monolayer and, as such, is proportional to the surface area. The c -value is related exponentially to an average energy of adsorption. In the conventional application of eq (1), the parameters a and b are evaluated from the experimentally obtained adsorption points (x, q) preferably by use of the method of least squares [8]. These "best" estimates of a and b are then used to obtain q_m and c . Finally, the surface area is obtained conventionally by multiplying q_m by an appropriate constant sometimes referred to as the "packing factor."

Most laboratory workers in surface chemistry are painfully aware of the fact that the good linearity of eq (1) is destroyed when the experimentally determined initial weight of the sample is in error. One should, therefore, expect that *the* best straight line would result only when a zero-point weight very close to the correct value is used in the calculations. This criterion was employed in the present investigation for determining the dry weight of a solid adsorbent when water vapor was the adsorbate. In other words, the humidified sample weights themselves, utilizing a least-squares technique, were permitted to determine that value of the dry weight, p , along with the usual two parameters a and b required to optimize the linearity:

If W_i represents the weight (in grams) of the sample at the i th point corresponding to a relative humidity x_i , the number of moles of water vapor adsorbed per g of dry adsorbent would be

$$q_i = \frac{W_i - p}{18p} \quad (3)$$

The value of x_i is assumed to be error-free here as it is in the conventional derivation.

The residual, R_i , is the experimental error of the ordinate of the i th point as indicated by the difference

$y_i - (a + bx_i)$. Equations (1), (2), and (3) may be combined to yield:

$$R_i = \frac{18x_i p}{(1-x_i)(W_i-p)} - (a + bx_i) \quad (4)$$

It is required to determine the values of the three parameters p , a , and b for which the sum of the squares of the residuals is a minimum.²

This amounts to solving three nonlinear simultaneous equations for these parameters given by eqs (5), (6), and (7):

$$\frac{\partial}{\partial p} \left[\sum_{i=1}^n R_i^2 \right] = 0 \quad (5)$$

$$\frac{\partial}{\partial a} \left[\sum_{i=1}^n R_i^2 \right] = 0 \quad (6)$$

$$\frac{\partial}{\partial b} \left[\sum_{i=1}^n R_i^2 \right] = 0 \quad (7)$$

By taking the partial derivative of the summation with respect to p as indicated by eq (5), the result is eq (8):

$$a \sum_{i=1}^n \frac{x_i W_i}{(1-x_i)(W_i-p)^2} + b \sum_{i=1}^n \frac{x_i^2 W_i}{(1-x_i)(W_i-p)^2} - 18p \sum_{i=1}^n \frac{x_i^2 W_i}{(1-x_i)^2 (W_i-p)^3} = 0 \quad (8)$$

In the same way, eqs (6) and (7) give rise to eqs (9) and (10), respectively.

$$an + b \sum_{i=1}^n x_i = 18p \sum_{i=1}^n \frac{x_i}{(1-x_i)(W_i-p)} \quad (9)$$

$$a \sum_{i=1}^n x_i + b \sum_{i=1}^n x_i^2 = 18p \sum_{i=1}^n \frac{x_i^2}{(1-x_i)(W_i-p)} \quad (10)$$

A cursory inspection of eqs (8), (9), and (10) discloses that the nonlinearity is ascribable entirely to the unknown parameter, p . In fact, the terms to the left of the equals signs in eqs (9) and (10), respectively, are identified with those obtained [8] in the "normalized" equations during the derivation of the least-square solution for a linear system. This observation suggests a relatively simple method for the simultaneous solution of eqs (8), and (9), and (10) for the parameters p , a , and b . An initial value p_1 is selected for p which is not quite as large as the lowest value of W_i . This value of p is substituted in eqs (9) and (10)

² This is rigorously valid only when the error represented by R_i has a normal (Gaussian) distribution over its entire range. Experience has confirmed that in the present application, this assumption is reasonably well approximated.

making it possible to solve them simultaneously for a and b which are then designated a_1 and b_1 , respectively. The values of a_1 , b_1 , and p_1 are then substituted in the left side of eq (8). The resultant value is called Φ_1 .

Since p_1 was initially selected to be somewhat high, it is decreased by a small predetermined amount to obtain its second iterative value, p_2 . Corresponding values of a_2 and b_2 are again calculated from eqs (9) and (10), as before, and all three contribute to the determination of Φ_2 from eq (8). If Φ_2 has the same sign as Φ_1 , it should be smaller in absolute value and the iterative process is repeated until there is a change in sign of Φ . At that point the incremental change in p is reduced to one-tenth of its previous value and its sign is automatically reversed. Again, the new direction is maintained with the smaller increment until the next change in sign of Φ is encountered. The process is repeated until negligible changes are obtained in successive values of p , a , and b while successive values of Φ approach zero in the limit. Usually this occurs within about 25 iterations and gives an estimate of surface area and goodness of fit as well as the dry weight of the sample.

The entire process has been programmed for computer operation (FORTRAN IV) and is given in the appendix (fig. A1) in a form used with a teletype time-sharing terminal.³

The values for the slope and the intercept were combined in the usual way at the end of each iteration by taking the reciprocal of their sum to obtain q_m . The factor $7.529 \times 10^4 \text{ m}^2/\text{mol}$ was used [10] to convert q_m to surface area. Only the final value, however, after convergence was complete could be considered valid.

(2) The Harkins and Jura (H-J) isotherm equation.

A linear relationship based on a two-dimensional equation of state was proposed by Harkins and Jura [3]. It took the form

$$\omega = \frac{A}{q^2} - B \quad (11)$$

where

$$\omega = \ln(1/x) \quad (12)$$

while A and B are constants.

There are no relative humidity restrictions on its range of applicability. (This is in contrast to the more familiar BET equation valid only within the inclusive values from about 0.1 to 0.3.) The surface area applicable to the H-J equation is proportional to the square root of the parameter A . The proportionality constant is, of course, dependent upon the adsorbate and the

temperature of the isotherm. The value used in this work corresponding to water vapor at 23 °C was $5.620 \times 10^4 \text{ m}^2/\text{mol}$ [12].

Using the same procedure described for the BET theory, the least square normalized equations resulting from the H-J isotherm equation are:

$$\Phi = Ap \left\{ \sum_{i=1}^n \frac{W_i \omega_i}{(W_i - p)^3} - (18)^2 Ap^2 \sum_{i=1}^n \frac{W_i}{(W_i - p)^5} + B \sum_{i=1}^n \frac{W_i}{(W_i - p)^3} \right\} \quad (13)$$

$$(18)^2 p^2 A \sum_{i=1}^n \frac{1}{(W_i - p)^2} - Bn = \sum_{i=1}^n \omega_i \quad (14)$$

$$(18)^2 p^2 A \sum_{i=1}^n \frac{1}{(W_i - p)^4} - B \sum_{i=1}^n \frac{1}{(W_i - p)^2} = \sum_{i=1}^n \frac{\omega_i}{(W_i - p)^2}. \quad (15)$$

The iterative procedure previously described was again resorted to and a computer program given in appendix (fig. A2) was tailored to accommodate the H-J equation. This resulted in converged estimates of dry weight and surface area while at the same time affording a measure of goodness of fit.

(3) Other Isotherm Equations

The Polarization Equation of deBoer and Zwikker [9]:

$$q = a' + b' \ln \omega \quad (16)$$

and the Polanyi Potential Theory [9]:

$$q = a'' + b'' \omega^{-1/3} \quad (17)$$

were both subjected to the same treatment as described for the other two theories and will be discussed in a later section.

3. Equipment and Procedures

The gravimetric adsorption equipment employed used a circulatory flow system and a means for supplying water vapor at predetermined humidities to the carrier gas as described in a recent publication [10]. A drying tube mounted vertically and filled with P_2O_5 supported on glass wool had a trap sealed to its lower end for holding back the phosphoric acid produced and isolating it from the gas stream during desiccation of a sample. The drying step was carried out at room temperature (23 °C) as were all of the humidity exposures. Drying was performed either initially or at the end of a humidity sequence, depending upon whether it was an adsorption or desorption series. The zero-humidity data were, of course, not used in the calculations and served only as experi-

³The Control Data "KRONOS" System (6000 series) high-speed digital computer required only about 1/4 s in a typical computation. The central computer time can be further shortened to about 1/5 s when several independent determinations are performed, since the compiling time (c.a. 1 s) need not be repeated. Similar results were obtained using the Sperry Rand "UNIVAC 1108" System.

Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

mental verification of the calculated values. Saturated salt solutions were used for obtaining the desired humidities, details of which were described previously [10]. However, any standard commercial equipment would work equally well in order to apply the technique in any particular case.

The order in which the experimental points are obtained is extremely important. They must be in a continually decreasing (desorption or drying) or in a continually increasing (adsorption) sequence to avoid hysteresis scanning loops [11].

Table 5 shows that even low area adsorbents respond well in dry weight prediction regardless of whether adsorption or desorption data are used.

The dry weights predicted in table 6 are significant because most of the data were collected at relative humidities above 50 percent. The ability to do this is especially valuable in nondestructive testing where complete dehydration might cause irreversible changes in the sample.

4. Results

Tables 1 through 6 summarize the results of several determinations. The grouping of the experiments helps to emphasize the capabilities as well as the limitations inherent in the method.

Most of the examples in table 1 give reasonably good agreement in surface area between BET and H-J. The experimentally measured dry weights, in the majority

of cases, are slightly greater than the calculated values. This suggests the possibility that the last traces of physically adsorbed water may not have been completely removed by the experimental procedure used. In one instance this effect is rather striking.⁴

The two experiments involving barium glass⁵ (water extracted) represent the initial and final adsorption sequence in an adsorption-desorption-adsorption cycle in which the relative humidity started at zero—went stepwise to saturation—then down to zero—and finally back up again to 0.334.

Good agreement between surface area predicted from desorption data with that from adsorption is not generally to be expected. Table 2 shows exceptions occur where hysteresis is either absent entirely or negligibly small.

Some insight may be deduced from the results of both isotherm equations even when only desorption (drying) data are available. Fair agreement between the “areas” as shown in the latter two examples of table 3 where hysteresis is known to be virtually nonexistent suggests that these values may be reasonably valid estimates of the true surface area.

Table 4 is self explanatory and shows consistency of both surface areas and predicted dry weights between widely different portions of the adsorption isotherm.

⁴ See Cellulose Acetate Membrane (table 4).

⁵ Corning Glass Company X95-1FD.

TABLE 1. *Adsorption*
Low humidity range (0.082 → 0.334)
Comparison of BET with H-J for the Same Data

Expt. No.		Surface area	Dry weight
		(m ² /g)	(g)
A503094	Synthetic Hydroxyapatite (6 points)		
	Calculated:		
	BET.....	47.2	0.2708
	H-J.....	44.4	.2717
	Experimental.....		.2733
A444168	Activated Bentonite (5 points)		
	Calculated:		
	BET.....	181.4	.7161
	H-J.....	182.5	.7193
	Experimental.....		.7378
A444161	Polycarboxylate Cement (4 points)		
	Calculated:		
	BET.....	60.4	1.255
	H-J.....	61.3	1.241
	Experimental.....		1.249
A444143	Zinc Phosphate Cement (6 points)		
	Calculated:		
	BET.....	41.8	1.5646
	H-J.....	32.4	1.5703
	Experimental.....		1.5779

TABLE 1. Adsorption—Continued

Expt. No.		Surface area	Dry weight
		(m ² /g)	(g)
A444155	<u>Barium Glass— as received (6 points)</u>		
	<u>Calculated:</u>		
	BET.....	3.22	1.2886
	H-J.....	3.15	1.2889
	<u>Experimental.....</u>		1.2895
A444156	<u>Barium Glass— Water Extracted (4 points)</u>		
	<u>Calculated:</u>		
	BET.....	8.7	0.9636
	H-J.....	4.6	.9648
	<u>Experimental.....</u>		.9649
A444175	<u>Barium Glass— Water Extracted (6 points)</u>		
	<u>Calculated:</u>		
	BET (no convergence).....		—
	H-J.....	9.5	.9646
	<u>Experimental.....</u>		.9657
A444164	<u>Zinc Oxide-Eugenol Cement (4 points)</u>		
	<u>Calculated:</u>		
	BET (no convergence).....		—
	H-J.....	5.2	3.1274
	<u>Experimental.....</u>		3.1297

TABLE 2. Adsorption versus desorption

Expt. No.	Hysteresis: Absent or minimal	Surface area	Dry weight
		(m ² /g)	(g)
A444065	<u>Poly(methyl methacrylate) (Low Humidity range 0.082 → 0.334)</u>		
	<u>Adsorption (5 points)</u>		
	<u>Calculated:</u>		
	BET.....	30.4	3.5029
	H-J.....	24.9	3.4878
A444064	<u>Desorption (6 points)</u>		
	<u>Calculated:</u>		
	BET.....	(31.6)	3.5022
	H-J.....	(29.4)	3.4847
	<u>Experimental.....</u>		3.5039
A444136	<u>“BIO GEL” (commercial hydroxyapatite)</u>		
	<u>Adsorption (Intermediate Humidity range 0.312 → 0.804)</u>		
	<u>Calculated (4 points):</u>		
	BET (not applicable).....	—	—
	H-J.....	43.3	0.3788
A444138	<u>Desorption (High Humidity range 0.926 → 0.542)</u>		
	<u>Calculated (5 points):</u>		
	H-J.....	(47.2)	.3792
	<u>Experimental.....</u>		.3802

TABLE 3. Desorption

Low Humidity Range (0.334 → 0.082) Comparison of BET with H-J for the same data

Expt. No.		Surface area	Dry weight
		(m ² /g)	(g)
A444159	<u>Barium Glass – Water Extracted</u> (5 points)		
	<u>Calculated:</u>		
	BET.....	(9.2)	0.9639
	H-J.....	(2.3)	.9659
	<u>Experimental</u>9657
A503137	<u>NPG-GMA Coated HA</u> (6 points)		
	<u>Calculated:</u>		
	BET.....	(14.6)	.4808
	H-J.....	(12.6)	.4799
	<u>Experimental</u>4805
A444139	<u>“BIO GEL” (commercial hydroxyapatite)</u> (5 points)		
	<u>Calculated:</u>		
	BET.....	(40.5)	.3792
	H-J.....	(59.4)	.3784
	<u>Experimental</u>3811

TABLE 4. Adsorption

Low humidity versus high humidity

Expt. No.		Surface area (m ² /g)	Dry weight (g)
A503140	<u>Dentin</u>		
	<u>Calculated</u> (6 points 0.082 → 0.334)		
	BET.....	146	2.0202
	H-J (poor convergence).....	—	—
	<u>Experimental</u>		2.0671
A503078	<u>Calculated</u> (5 points 0.082 → 0.312)		
	BET (no convergence).....	—	—
	H-J.....	143	.2847
A503079	<u>Calculated</u> (4 points 0.334 → 1.000)		
	BET (not applicable).....	—	—
	H-J.....	150	.2848
	<u>Experimental</u>2898
A444148	<u>Cellulose Acetate Membrane</u>		
	<u>Calculated</u> (6 points 0.082 → 0.334)		
	BET.....	191	.06424
	H-J.....	176	.06480
A444149	<u>Calculated</u> (7 points 0.435 → 1.000)		
	BET (not applicable).....	—	—
	H-J.....	197	.06491
	<u>Experimental</u>06681

TABLE 5. Adsorption—desorption
High humidity range (0.435–0.971)

Expt. No.		Surface area (m ² /g)	Dry weight (g)
A444124	<u>Pulverized Dental Amalgam</u>		
	<u>Adsorption (7 points)</u>		
	<u>Calculated</u>		
	H-J.....	0.44	5.6135
A444126	<u>Desorption (4 points)</u>		
	<u>Calculated</u>		
	H-J.....	(0.74)	5.6132
	<u>Experimental</u>		5.6145

TABLE 6. High humidity drying (desorption) curves for predicting water content*

Expt. No.		Surface area (m ² /g)	Dry weight (g)
A444145	<u>Cellulose Acetate Membrane (Humidity Range 0.926 → 0.655)</u>		
	<u>Calculated (4 points): H-J</u>	(148.3)	.06645
	<u>Experimental</u>06681
A444153	<u>Barium Glass (Humidity Range 0.926 → 0.435)</u>		
	<u>Calculated (6 points): H-J</u>	(2.5)	1.28897
	<u>Experimental</u>		1.28947
A444158	<u>Extracted Barium Glass (Humidity Range 0.971 → 0.435)</u>		
	<u>Calculated (7 points): H-J</u>	(3.4)	.9663
	<u>Experimental</u>9657
A444171	<u>Activated Bentonite (Humidity Range 0.926 → 0.542)</u>		
	<u>Calculated (5 points): H-J</u>	(242)	.7113
	<u>Experimental</u>7378
A503091	<u>Commercial Synthetic Hydroxyapatite (Humidity Range 1.000 → 0.757)</u>		
	<u>Calculated (5 points): H-J</u>	(117)	.2612
	<u>Experimental</u>2733
A503136	<u>NPG-GMA Coated HA (Humidity Range 1.000 → 0.542)</u>		
	<u>Calculated (7 points): H-J</u>	(25)	.4788
	<u>Experimental</u>4805

*Other examples included in tables 2 and 5.

5. Discussion

The fact that the least-squares technique can be applied successfully for determining unbound water content along with surface area for the BET and the H-J isotherm equations raises the question of whether it would work equally well for other adsorption theories. Accordingly, computer programs were developed for testing the Potential theory and the Polarization theory, each of which could be expressed in linear form [9]. It soon became clear that this method would not be applicable to either one of these latter isotherm equations. They seemed to be "ill-conditioned" or not sufficiently sensitive to perturbation in sample weight to be of practical use in instances where both BET and H-J converge readily. Further testing was

therefore abandoned. The possibility remains that still other isotherm equations [2, 4, 5] (besides the four tested here) might well be adaptable to this technique.

It is instructive to assess the relative advantages of BET and of H-J as applied to the present work:

(1) The H-J would, of course, be used for all values beyond the relative pressure (about 0.3) of the applicable BET range.

(2) For very small surface area samples where the points in the BET range may be too erratic for successful convergence, the points higher up on the isotherm may have sufficiently reduced relative error to give successful convergence using H-J.

(3) In the valid BET region where both isotherm equations could be used, the BET equation appeared to be the more sensitive. When the experimental

error of the points was excessive, neither computer program would converge. At moderate error such that only one equation led to successful convergence it was usually H-J (see tables 1 and 4).

(4) In many instances where no convergence was found when using the BET equation, a minimum in the residual variance (mean-square deviation of the ordinates of the experimental points from the assumed curve) was useful as a rough estimate of the correct dry weight and surface area.

(5) When convergence was attained using both isotherm equations and the predicted surface areas were in reasonably good agreement (see first four experiments in table 1), it served to reinforce one's confidence in the validity of the results. When agreement was somewhat less than desired for a homogeneous adsorbent (see table 1, Expt A444156), the BET value would be preferred. Note that the BET surface area value of 8.7 m²/g (rather than the H-J value of 4.6) was in better agreement with the results of Experiment A444175 for the same adsorbent (also table 1) for which the H-J value of 9.5 m²/g was calculated.

(6) For a nonhomogeneous adsorbent where aggregate behavior might lead to an erroneous BET value [12] as a result of large differences in energies of adsorption among the components of the solid, the H-J area would always be preferable.

Throughout tables 2, 3, 5, and 6 surface area values obtained from desorption experiments are shown in parenthesis. They are likely to be erroneous unless the desorption curve is substantially a retracing of the adsorption curve (absence of hysteresis). This is a property of the adsorbent-adsorbate system and must be considered case by case. Virtual absence of hysteresis is portrayed by the materials listed in table 2 and exists to only a slight degree for those listed in table 3. The dry weight values, however, are just as valid with desorption as with adsorption provided the desorption originates at saturation resulting in a descending boundary curve [13]. Other instances which have been found to agree with the experimental results for dry weight include primary descending scanning curves; although the predicted surface area would not be valid. A case in point is illustrated by an experiment not shown in the tables. Water vapor was adsorbed on a desiccated sample of Bio Gel⁶ to a relative humidity of 0.804 after which seven additional successive desorption values were obtained. Convergence was successful using H-J resulting in a predicted dry weight of 0.3788 g compared with the experimental value of 0.3811 g obtained after taking the sample again to dryness.

Desorption along scanning curves other than those already mentioned as well as adsorption along scanning curves, will invariably result in erroneous values for dry weight prediction in spite of satisfactory convergence of the computer program. Two experiments performed with the same sample of human dentin will serve to illustrate this. In both cases, the starting

point was saturation (relative humidity = 1.00). In the first experiment (A444090), desorption occurred along the descending boundary curve to a value of 0.175 relative humidity. This was followed by adsorption along a primary ascending scanning curve to a relative humidity of 0.757. Desorption was next carried out stepwise along this secondary descending scanning curve. The sample weights measured were: 0.249303 g, 0.247758 g, 0.246568 g, and 0.245402 g at the corresponding relative humidities of 0.757, 0.655, 0.542, and 0.435, respectively. The dry weight predicted from using the H-J equation was 0.2356 g as compared with 0.2288 g measured experimentally. In the other experiment (A444091) the initial turning point between the descending boundary curve and the primary ascending scanning curve took place at 0.122 r.h. (instead of 0.175 r.h.). In this experiment, the sample weights at the same respective humidities along the secondary descending scanning curve were 0.248456 g, 0.247364 g, 0.245881 g, and 0.244989 g. These values gave rise to a predicted dry weight of 0.2369 g. It is significant that in both of these experiments the dry weight was predicted about four percent on the *high* side compared with the actual measurement. A detailed study of the behavior of scanning curves in adsorption-desorption hysteresis is beyond the scope of this paper [13].

It was stated earlier in this discussion (subparagraph 3) that the BET equation was extremely sensitive regarding the effect of experimental error on convergence of the computer program. If a sufficient number of points are available in a system in which the BET equation is known to be valid and yet the computer program does not converge, it is useful to plot the original data especially when it is impractical (or impossible) to repeat the experiment. If one of the points does not fit a smooth curve which passes through the remaining points, those remaining points may very well allow the computer program to converge. Of course, the results should be examined carefully for reasonableness of the predicted quantities before they are accepted. This suggestion is submitted in lieu of a valid test for outliers [14] in a system as complicated as this.

It is appropriate to caution the reader that the method described in this paper is *not* proposed as a substitute for measuring the zero humidity point in routine surface area determinations. It is also entirely feasible that experimental errors might combine in such a way as to permit convergence and yet yield incorrect results. In other words, the need for careful experimental work is probably even more important when the additional demand is placed on the sorption points to estimate the zero humidity value as well as the surface area.

Some applications in which the methods described in this paper would be especially valuable are:

(1) Where routine measurements have yielded good linear BET results yet, now and then, a sample of the same type of material when plotted in accordance with eq (1) produced a curve instead of a straight line.

⁶ BIO-RAD Laboratories, Richmond, California.

In such instances, the entire experiment would normally have to be discarded and all because an error in the experimental determination of the dry weight was reflected in all the *other* points on the plot.

(2) Dry weight of materials that evolve gases during decomposition at low pressures.

(3) In agricultural products (such as grain) and other materials where the last traces of water may be extremely slow coming off during drying (desorption), provided again that the isotherm equation employed is known to be appropriate for that system.

(4) In biological applications where viability of the organism (or tissue) would be destroyed by complete drying while, perhaps, equilibration at, say, fifty percent relative humidity might be tolerated, non-destructive determinations of dry weight could be made. This would be especially useful in growth rate studies.

(5) In situations where no other method may be available for estimation of dry weight and/or surface area from previously obtained data which may be incomplete.

6. Summary

(1) It has been demonstrated that adsorption or desorption data are capable of estimating the unbound water content of solid adsorbents. This was accomplished by the convergence of a computer program which employed a least-squares technique applied to an appropriate isotherm equation.

(2) The Brunauer, Emmett, and Teller free surface equation and the Harkins and Jura equation were readily adaptable to this treatment (the Polarization equation and the Potential theory equation did not respond).

(3) A valid estimate of surface area was also obtained when data from adsorption experiments were used or with such desorption experiments for which no hysteresis existed. Where there was hysteresis, the predicted surface area while incorrect was a useful order-of-magnitude estimation, usually as an upper limit.

(4) Applications of the technique for determining the dry weights were compared with experimentally measured values for solids which cover a wide range in surface area. The agreement was within about one percent and the calculated dry weight was usually on the low side.

(5) The capabilities as well as the limitation in the application of these methods were compared and discussed.

7. Appendix. Procedure for Using Isotherm Data With Time Sharing Teletype Terminal

Fortran Computer programs are given in figure A1 for the BET equation in figure A2 for the Harkins and

Jura equation. A minimum of four data points is required, although a larger number is preferred. The adsorption (or desorption) data can be pre-punched on paper tape before connecting the terminal with the computer. (The input format has been designed such that the same data tape may be used with either program.) A typical data file, for example, (A444153) transposed from the tape is shown in table A1. The initial line (here designated as 10) contains:

- a. The number of data points in the experiment (in this case, 6).
- b. The maximum number of iterations.
- c. A starting value (tentative) for the dry weight.
- d. The initial decrement (or amount by which the preceding numeral is changed in initiating the iterative process).

Subsequent lines of table A1 contain the sample weight along with the corresponding humidity to which the sample was exposed until that steady-state weight had been attained.

The order of the points in table A1 indicates in this illustration that a desorption process originating at a relative humidity of 1.00 was measured initially at 0.926 r.h., and finally at 0.435. While a maximum of 33 iterations was provided for in this example, only about 20 were needed before no further change of any consequence resulted.

TABLE A1. *Input data for Expt. A444153*

10	06	33	01.289000	-0.000400
11	01.294267	0.926		
12	01.291396	0.804		
13	01.290930	0.757		
14	01.290616	0.655		
15	01.290353	0.542		
16	01.290112	0.435		

The initiating value of 01.289000 g was chosen to be less than any of the data points and yet obviously greater than the expected dry weight. The choice of -0.000400 for the weight change meant that a value of 1.288600 g for a tentative dry weight would be tested by the computer in its next iteration. The Harkins and Jura program (HARJUR) would, of course, be used for the data file A444153, since the humidities are beyond the valid range applicable to the BET theory.

In the course of the computer run the value of Φ must change signs repeatedly as it converges toward zero. This is a necessary criterion for a successful determination. The value predicted for dry weight for this particular set of data was 1.28897 g while the predicted ⁷ surface area was 2.49 m²/g. (Other columns present in the computer printout (not shown here) represent intermediate steps in the calculations or estimate the goodness of fit to the linear form of the isotherm equation.)

An interesting application of the computer program is the degenerate case where the iterations are suppressed. This would occur when the dry weight is

⁷ The predicted surface area would normally *not* be valid in the case of a desorption experiment (such as this) unless hysteresis was absent. It is useful, however, as an estimate of the order of magnitude of the surface area.

```

00010 PROGRAM WASSER (INPUT,OUTPUT,TAPE1)
00020*THIS PROGRAM IS DESIGNED TO FIND THE DRY WEIGHT P(JJ) WHERE
00030*X(I) IS THE RELATIVE HUMIDITY, V(I) IS THE WEIGHT OF SAMPLE
00040*AT EQUILIBRIUM WITH X(I), AND J IS THE ITERATION OF THE PAR-
00050*AMETER. MAX I IS II. MAX J IS JJ. THE VALUE OF II
00060*MUST BE AT LEAST 4. THE RANGE OF X(I) SHOULD BE 0.08 TO 0.33.
00070 DIMENSION V(50), X(50), P(99), F3(50), F4(50), F5(50),
00080+ F6(50), F8(50)
00090 READ (1,61) II, JJ, P(1), DELP
00100 61 FORMAT (3X, I2, 1X, I2, 1X, F9.6, 1X, F9.6)
00110 PRINT 62
00120 62 FORMAT (/3X, 2HII, 1X, 2HJJ, 5X, 4HP(1), 7X, 4HDELP//)
00130 PRINT 61, II, JJ, P(1), DELP
00140 READ (1,63) (V(I), X(I), I=1,II)
00150 63 FORMAT (3X, F9.6, 1X, F5.3)
00160 PRINT 64
00170 64 FORMAT (///5X, 4HV(1), 5X, 4HX(I)///)
00180 PRINT 63, (V(I), X(I), I=1,II)
00190 PRINT 65
00200 65 FORMAT (////1X, 1HJ, 6X, 4HP(J), 8X, 3HPHI, 9X, 1HA, 9X,
00210+ 1HE, 8X, 4HAREA, 7X, 10HMN SQR DEV//)
00220 AII = II
00230 PPEPHI = 0.0
00240 DO 104 J=1, JJ
00250 GX2 = 0.0
00260 DO 92 I=1, II
00270 92 GX2 = GX2 + X(I)**2
00280 GX = 0.0
00290 DO 94 I=1, II
00300 94 GX = GX + X(I)
00310 DEN = AII*GX2 - GX**2
00320 DO 111 I=1, II
00330 111 F3(I) = X(I)/(1.0-X(I))/(V(I)-P(J))
00340 GF3 = 0.0
00350 DO 112 I=1, II
00360 112 GF3 = GF3 + F3(I)
00370 DO 113 I=1, II
00380 113 F4(I) = X(I)*F3(I)
00390 GF4 = 0.0
00400 DO 114 I=1, II
00410 114 GF4 = GF4 + F4(I)
00420 DO 115 I=1, II
00430 115 F5(I) = F3(I)*V(I)/(V(I)-P(J))
00440 GF5 = 0.0
00450 DO 116 I=1, II
00460 116 GF5 = GF5 + F5(I)
00470 DO 117 I=1, II
00480 117 F6(I) = X(I)*F5(I)
00490 GF6 = 0.0
00500 DO 118 I=1, II
00510 118 GF6 = GF6 + F6(I)
00520 DO 119 I=1, II
00530 119 F8(I) = F3(I)*F5(I)
00540 GF8 = 0.0
00550 DO 120 I=1, II
00560 120 GF8 = GF8 + F8(I)
00570 A = 18.0*P(J)*(GX2*GF3 - GX*GF4)/DEN
00580 E = 18.0*P(J)*(AII*GF4 - GX*GF3)/DEN
00590 AREA = 7.529E+04/(A+E)
00600 PHI = A*GF5 + E*GF6 - 18.0*P(J)*GF8
00610 SSQRS = 0.0
00620 DO 4 I=1, II
00630 4 SSQRS = SSQRS + (V(I) - P(J))*(1.0 + 18.0*X(I)/
00640+ (1.0 - X(I)))/(A + E*X(I))**2
00650* SSQRS OF DEVS OF V(I) FROM CURVILINEAR REGRESSION
00660 VAR = SSQRS/(AII - 3.0)
00670 PRINT 99, J, P(J), PHI, A, E, AREA, VAR
00680 99 FOFMAT (I2, 2E13.5, 2E10.2, 2E12.4)
00690 IF (PHI*PPEPHI) 95,96,96
00700 95 DELP = -0.1*DELP
00710 96 PPEPHI = PHI
00720 P(J+1) = P(J) + DELP
00730 104 CONTINUE
00740 STOP
00750 END

```

FIGURE A1. Computer Program, WASSER, (FORTRAN IV) for determination of unbound water content (dry weight) and Surface Area from water vapor sorption data according to the BET adsorption theory.

```

00010 PROGRAM HAFJUR(INPUT,OUTPUT,TAPE1)
00020*THIS PROGRAM IS DESIGNED TO FIND THE DRY WEIGHT P(JJ)
00030*WHERE X(I) IS THE RELATIVE HUMIDITY, W(I) IS THE
00040*WEIGHT OF SAMPLE AT EQUILIBRIUM WITH X(I), AND J IS THE
00050*ITERATION OF THE PARAMETER. MAX I IS II. MAX J IS JJ.
00060*THE VALUE OF II MUST BE AT LEAST 4.
00070 DIMENSION V(50), X(50), P(99), H1(50), H2(50)
00080 READ(1,61) II, JJ, P(1), DELP
00090 61 FORMAT (3X, I2, 1X, I2, 1X, F9.6, 1X, F9.6)
00100 PRINT 62
00110 62 FORMAT (/3X, 2HII, 1X, 2HJJ, 5X, 4HF(1), 7X, 4HDELP//)
00120 PRINT 61, II, JJ, P(1), DELP
00130 READ(1,63) (W(I), X(I), I=1, II)
00140 63 FORMAT (3X, F9.6, 1X, F5.3)
00150 PRINT 64
00160 64 FORMAT (///5X, 4HW(I), 5X, 4HX(I)///)
00170 PRINT 63, (W(I), X(I), I=1, II)
00180 PRINT 65
00190 65 FORMAT (///1X, 1HJ, 6X, 4HP(J), 8X, 3HPHI, 9X,
00200+ 1HA, 9X, 1HE, 8X, 4HAFAEA, 7X, 10HMN SQR DEV///)
00210 AII = II
00220 PREPHI = 0.0
00230 DO 104 J = 1, JJ
00240 DO 90 I = 1, II
00250 90 H1(I) = ALOG(1.0/X(I))
00260 GH1 = H1(I)
00270 DO 91 I = 2, II
00280 91 GH1 = GH1 + H1(I)
00290 DO 92 I = 1, II
00300 92 H2(I) = 1.0/(W(I) - P(J))
00310 GH2 = H2(I)**2
00320 DO 93 I = 2, II
00330 93 GH2 = GH2 + H2(I)**2
00340 GH12 = H1(I)*H2(I)**2
00350 DO 94 I = 2, II
00360 94 GH12 = GH12 + H1(I)*H2(I)**2
00370 GH4 = H2(I)**4
00380 DO 95 I = 2, II
00390 95 GH4 = GH4 + H2(I)**4
00400 GHV3 = W(I)*H2(I)**3
00410 DO 96 I = 2, II
00420 96 GHV3 = GHV3 + W(I)*H2(I)**3
00430 GH1V3 = W(I)*H1(I)*H2(I)**3
00440 DO 97 I = 2, II
00450 97 GH1V3 = GH1V3 + W(I)*H1(I)*H2(I)**3
00460 GHV5 = W(I)*H2(I)**5
00470 DO 98 I = 2, II
00480 98 GHV5 = GHV5 + W(I)*H2(I)**5
00490 DEN = (18.0*P(J))**2*(AII*GH4 - GH2**2)
00500 ANUM = AII*GH12 - GH1*GH2
00510 A = ANUM/DEN
00520 ENUM = (18.0*P(J))**2*(GH2*GH12 - GH1*GH4)
00530 E = ENUM/DEN
00540 PHI = A*P(J)*(GH1V3 - A*(18.0*P(J))**2*GHV5 + E*GHV3)
00550 SSQRS = 0.0
00560 DO 4 I = 1, II
00570 4 DISC = A/(H1(I) + E)
00580 IF (DISC) 70, 69, 69
00590 69 DSCR = DISC
00600 SSQRS = SSQRS + (W(I)-P(J))*(1.0+18.0*SQRT(DSCR))**2
00610 GO TO 4
00620 70 SSQRS = 1.0E+08
00630 4 CONTINUE
00640* SSQRS OF DEVS OF V(I) FROM CURVILINEAR REGRESSION
00650 VAF = SSQRS/(AII-3.0)
00660 IF (A.LT.0.0) GO TO 111
00670 AREA = 5.62E+04*SQRT(A)
00680 GO TO 112
00690 111 AREA = 0.0
00700 112 PRINT 99, J, P(J), PHI, A, E, AREA, VAF
00710 99 FORMAT (I2, 2E13.5, 2E10.2, 2E12.4)
00720 IF (J.EQ.1) GO TO 101
00730 IF (PHI*PREPHI) 100, 100, 101
00740 100 DELP = -0.1*DELP
00750 101 PREPHI = PHI
00760 P(J+1) = P(J) + DELP
00770 104 CONTINUE
00780 STOP
00790 END

```

FIGURE A2. Computer Program, HARJUR, (FORTRAN IV) for determination of unbound water content (dry weight) and Surface Area from water vapor sorption data according to the H-J adsorption theory.

available experimentally along with the rest of the data points and the experimenter is primarily interested in the least-squares value of the surface area. In the first line of the input data file (table A1) he would set the number of iterations equal to 01 and would insert the known dry weight for the initial value of p which is the next entry on that same first line. The final entry (corresponding to the initial decrement) while it will be ignored by the computer should, never-the-less, be present even if all its digits are zeroes.

The computer programs used in this work are reproduced in figures A1 and A2.

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