Multimolecular Adsorption Equation

R. R. ROUNSLEY
The Mead Corporation, Chillicothe, Ohio

An equation is derived for the multimolecular adsorption isotherm in the range where capillary adsorption is insignificant. The equation is demonstrated to apply quantitatively to the entire range of relative vapor pressures. It is shown that this equation reduces to the equation of Brunauer, Emmett, and Teller at lower relative vapor pressures.

Application of this equation to data in the literature showed good agreement. The standard deviation of the data from the equation was in the same order of magnitude as the scatter of the data themselves. Although the application of this equation was largely to water vapor adsorption systems, several applications to other systems correlated equally well.

MULTIMOLECULAR ADSORPTION EQUATION

In the conditioning of such materials as paper, textiles, or wood it would be a significant help to be able to describe the adsorption isotherm with a minimum of effort.

During the later stages of drying of hygroscopic materials the drying rate and the final moisture content depend upon the amount of water which is adsorbed on the material at a given partial pressure. It would be of considerable value to be able to describe the adsorption isotherm with a single equation.

Because of the large amount of time consumed in determining any adsorption isotherm, it would be invaluable to be able to extrapolate the entire adsorption isotherm from as few data as possible.

A number of attempts to describe adsorption isotherms have been successful over a portion of the humidity range. The earlier equation of Langmuir (*1*) has been found to qualitatively describe monomolecular adsorption over the entire range of humidities and multimolecular adsorption of many systems in the low partial-pressure range. The Brunauer, Emmett, and Teller (B.E.T.) equation (*2*) has been quantitatively very successful up to a relative vapor pressure of 0.5 and occasionally higher. The empirical methods, such as that of Harkins and Jura (*3*), have met with limited success but do not apply to as wide a range as the B.E.T. equation. The Flory treatment for polymer solutions, on the other hand, shows good agreement in the high relative vapor-pressure range (*4*).

None of these however may be applied over the entire range of humidities. This makes extrapolation of measured data for adsorption isotherms extremely tenuous. It would be especially convenient to be able to describe the isotherm for water vapor adsorption systems, since these are commonly encountered in practice. For these systems the entire range of humidities will be experienced.

Several stages in the adsorption process are found in going from zero partial pressure to saturation. The first molecules are adsorbed on localized sites with considerable energy of adsorption. As the number of adsorbed molecules increases, second and successive layers begin to form. These molecules are in a very mobile condition. Their energy of adsorption is roughly equal to the heat of condensation. Finally in a porous material, when the partial pressure becomes sufficiently high, condensation will occur in the capillaries because of the reduction in vapor pressure over a concave surface.

The first two stages are determined by the properties of the adsorbing solid, while the last is determined only by the pore size distribution. Although it is not intended to include capillary condensation in this analysis, its effect may be estimated from a knowledge of the pore size distribution. For most of the materials considered capillary condensation was insignificant below 0.95 relative vapor pressure.

Hysteresis effects are quite prominent in many adsorption isotherms; that is the equilibrium humidity for a given moisture content is higher on adsorption than on desorption. The usual hysteresis loop is shown in Figure 1. The presence of air or other impurities increases this effect, so that a minimum hysteresis is obtained when the adsorbent has been degassed thoroughly by evacuation at higher temperature (*5*). This will leave a nonswelling material with only the hysteresis caused by capillary condensation which cannot be eliminated. Unfortunately, this precaution has not been observed in the data of most of the authors cited in this paper. This is not unusual, since the use of many materials precludes such an artificial treatment as degassing.

Derivation of Equation

Fowler and Guggenheim (*1*) and Cassie (*6*) have demonstrated the success of a statistical derivation of adsorption isotherms. A simplified statistical thermodynamic derivation is presented here showing only the most important points of the derivation. The following assumptions were made in this derivation:

1. The energy of adsorption of the first layer is measurably different from that of the other layers.
2. The energy of adsorption of all but the first layer remains constant and equal to the energy of condensation.
3. There is no appreciable energy of interaction between adjacent molecules adsorbed on the surface.
4. The distribution of molecules among the different layers builds up during adsorption in an efficient, orderly manner.
5. The adsorption surface or number of adsorption sites is constant.
6. The number of layers that can form is limited.
7. The vapor behaves as an ideal gas.

The first three assumptions are commonly assumed in an adsorption process. Assumption four however characterizes this derivation; it prevents a random buildup of layers, since the number in each layer will depend upon the number already present in the underlying layer. Because of the high mobility of the molecules in the upper layers one would expect such a dependence to be necessary.

Assumption five would appear to be invalid, since the surface of most of the materials tested is known to swell considerably on adsorption. Ledoux (*5*) on the other hand indicates that it would be more appropriate to say that the adsorbent contracts on desorption because the volume is considered to be normal under no strain. Furthermore the contraction frequently results in a change in the number of adsorption sites available. Therefore this poses some difficulties when one uses the adsorption isotherm to estimate surface areas.

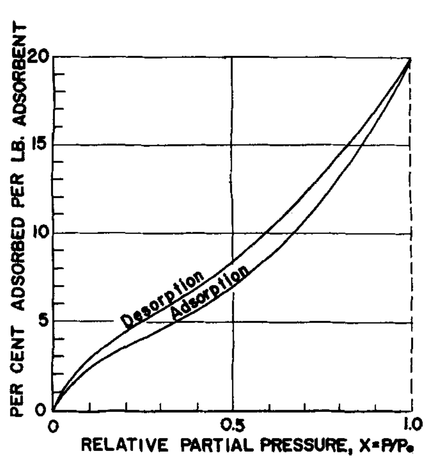

Fig. 1. Typical adsorption-desorption isotherm showing hysteresis loop.

The limit to the number of layers was at first considered to be only a function of the pore size distribution and structure (2), but, as pointed out by Joyner, Weinberger, and Montgomery (3), this assumption must include more than just these geometric limitations.

At the pressures encountered here, assumption seven appears to be justified.

Consider a solid having N_0 sites available for adsorption. First put N_1 molecules in the first layer. This can be done in W_1 ways:

$$W_1 = \frac{N_0!}{N_1!(N_0 - N_1)!} \qquad (1)$$

For the outermost molecules of the i^{th} layer

$$W_i = \frac{N_{i-1}!}{N_i!(N_{i-1} - N_i)!} \qquad (2)$$

If each layer has an energy of adsorption, the partition function $J = je^{E_a/RT}$ for each layer must be included. The over-all partition function for a completed layer becomes

$$Q_i = \frac{N_{i-1}!\ \ J_i N_i}{N_i!(N_{i-1} - N_i)!} \qquad (3)$$

One is interested however in only the most probable distribution between layers (assumption 4). This may be satisfied by $\delta Q_i/\delta N_i = 0$ or $\delta \ln Q_i/\delta N_i = 0$ for all possible layers. Using the Stirling approximation for the factorial of large numbers one obtains

$$\frac{\delta \ln Q}{\delta N_i} = -\ln \frac{N_i}{(N_{i-1} - N_i)J_i} = 0 \qquad (4)$$

Then

$$\frac{N_1}{N_0 - N_1} = \frac{J_1}{J_2}\left[\frac{N_2}{N_1 - N_2}\right] = \frac{J_1}{J_3}\left[\frac{N_3}{N_2 - N_3}\right] = \ldots \frac{J_1}{J_i}\left[\frac{N_i}{N_{i-1} - N_i}\right] \qquad (5)$$

Now let

$$\frac{N_1}{N_0 - N_1} = Cz \qquad (6)$$

and in accordance with assumption 2, $J_2 = J_3 = \ldots\ J_i$; thus

$$C = \frac{J_1}{J_i} \qquad (7)$$

Then

$$z = \frac{N_2}{N_1 - N_2} = \frac{N_3}{N_2 - N_3} = \ldots\ldots \frac{N_i}{N_{i-1} - N_i} \qquad (8)$$

and

$$N_i = \frac{N_0 C z^i}{(1 + z)^{i-1}(1 + Cz)} \qquad (9)$$

The total amount adsorbed is

$$N_t = \sum_{i=1}^{i=n} N_i = \frac{CN_0 z}{1 + Cz} \sum_{i-1}^{i=n} \left[\frac{z}{1 + z}\right]^{i-1} \qquad (10)$$

where n is the maximum number of layers which can be adsorbed. Noting that the summation term is a geometric series, by adding n terms, one can obtain after simplifying

$$N_t = \left[\frac{CN_0 z}{(1 + Cz)}\right](1 + z)\left[1 - \left(\frac{z}{1 + z}\right)^n\right] \qquad (11)$$

The over-all partition function for all of the layers is the product of the partition functions for each layer. For the system Q becomes

$$Q = \frac{N_0!}{N_n!}\prod_{i=1}^{i=n} \frac{J_i^{N_i}}{(N_{i-1} - N_i)!} \qquad (12)$$

TABLE 1. MATERIAL FOR WHICH ADSORPTION ISOTHERMS WERE DETERMINED

Material	Source
Adsorption of water	
Cotton, cellulose	*7, 8, 9, 10, 11*
Cellulose derivatives	*11, 12, 13*
Drierite	*14*
Lignin	*15*
Nylon	*12*
Polyvinyl alcohol	*12*
Proteins	*16, 17, 18*
Pulp and paper	*15, 19, 20, 21, 22, 23*
Silica gel	*24*
Silk	*11, 16*
Starch	*17*
Wood	*7, 15*
Wool	*11, 16, 25*
Adsorption of nitrogen	
$Al_2O_3 \cdot SiO_2$	2, 3
Anatase	3
Carbon	3

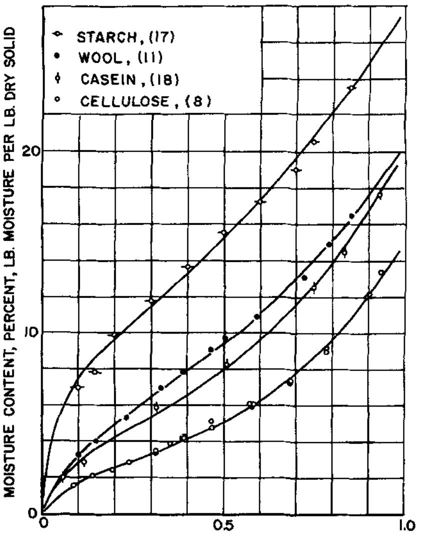

Fig. 2. Correlation of various adsorption isotherms by the new adsorption equation (solid lines represent equation correlation).

From this the free energy and chemical potential for the system may be calculated:

$$\frac{F}{kT} = -\ln Q = N_n \ln N_n - N_0 \ln N_0 + \sum_{i=1}^{i=n} (N_{i-1} - N_i)\ln(N_{i-1} - N_i) - N_i \ln J_i \qquad (13)$$

$$\frac{\mu_i}{kT} = \frac{\delta}{\delta N_i}\left[\frac{F}{kT}\right] = \ln(N_i - N_{i+1}) - \ln(N_{i-1} - N_i) - \ln J_i \qquad (14)$$

This μ_i/kT must be equal to μ/kT for the vapor phase. If this is a perfect gas (assumption 8), then

$$\frac{N_i - N_{i+1}}{N_{i-1} - N_i} = PJ_i\ e^{\mu_{og}/kT} = x \qquad (15)$$

The symbol x will be used in the rest of the derivation. Substituting Equation (9) in (15) one gets

$$x = \frac{z}{1 + z} \qquad (16)$$

and

$$z = \frac{x}{1 - x} \qquad (17)$$

Then when one substitutes Equation (17) in (11)

$$N_t = \frac{CN_0 x}{1 + (C - 1)x}\left[\frac{1 - x^n}{1 - x}\right] \qquad (18)$$

However N_0 and N_t are generally not known; only the amount adsorbed is known. Therefore substitute A and B:

$$A = \frac{BCx}{1 + (C - 1)x}\left[\frac{1 - x^n}{1 - x}\right] \qquad (19)$$

Method of Application

In order to correlate experimental data Equation (19) may be rewritten:

TABLE 2. SOME TYPICAL ADSORPTION CONSTANTS INCLUDING THOSE SHOWN IN THE FIGURES

Material and source	B	C	n	σ*	Figure number
Casein, (*18*)	4.53	11.11	4.40	0.31	2
Cellulose, (*8*)	2.85	10.67	5.29	0.22	2
Cellulose, typical	4.00	10.00	5.00		1
Cellulose, typical†	5.00	10.00	4.00		1
Envelope paper, (*19*)	2.75	14.69	4.42	0.36	
N_2 on anatase, (*3*)	3.24	100.9	3.99	0.46	
N_2 on Fe-Al_2O_3, (*2*)	133.0	156.7	∞	57.6	3I
N_2 on Fe-Al_2O_3, (*2*)	133.0	156.7	6.0	39.4	3II
N_2 on Fe-Al_2O_3, (*2*)	133.0	126.4	4.08	10.8	3III
Silica gel, (*24*)	17.65	2.27	2.52	0.98	
Starch,† (*17*)	8.86	2.68	3.11	0.46	2
Wood pulp,† (23)	5.43	5.01	6.61	0.23	
Wool,† (*11*)	5.69	9.38	3.56	0.24	2
Wool, (*11*)	4.04	8.98	4.74	0.18	

* σ given in same units as B, usually percent moisture on a dry basis.
† Desorption isotherm.

$$\frac{x(1-x^n)}{A(1-x)} = \frac{1}{BC} + \frac{(C-1)x}{BC} \tag{20}$$

Thus a plot of $x(1 - x^n)/[A(1 - x)]$ against x will give a straight line, provided n is known. If n is greater than 5, the term $(1 - x^n)$ remains essentially equal to unity when x is less than 0.5. The equation then reduces to the B.E.T. equation, and the evaluation of constants proceeds in the usual manner. It may be noted that with any value of n the new equation will approach the B.E.T. equation at sufficiently low values of x. Thus the slope and intercept may be easily found at lower values of x without a knowledge of n by plotting $x/[A(1 - x)] = Y_c$ against x. The higher humidity values will fall above the extrapolated value of Y_c in the ratio 1: $(1 - x^n)$.

Then n may be calculated for each point by

$$n_k = \frac{\log\,(1 - Y_e/Y_c)}{\log x} \tag{21}$$

where Y_e is the extrapolated value of Y_c from the lower humidity values.

Ideally n would be identical for all points. Practically, experimental error makes n less reliable as $(Y_c - Y_e)$ becomes small; therefore a weighted average based on $(Y_c - Y_e)$ is used to find the mean value of n:

$$n_{\text{mean}} = \frac{\Sigma(Y_c - Y_e)_k\, n_k}{\Sigma(Y_c - Y_e)_k} \tag{22}$$

The analyses of data presented here were made on an IBM-650 computer with a modified For Transit program and curve fitting routine.

For the data given here a second fit was made for the slope and intercept with Equation (20) and the previously determined value of n.

The values of B and C can then be computed by the following equations or their equivalent:

$$C = \frac{S}{I} + 1 \tag{23}$$

$$B = \frac{1}{I + S} \tag{24}$$

The value of the intercept for most of the data was usually very small. In most cases it was of the same order of magnitude as the standard deviation. In Equation (23) the intercept appears in the denominator of a ratio making the value of C so determined generally unreliable. Since it only appears as an additive value to the slope in the denominator of Equation (24), the accuracy of B should be determined primarily by the slope. The accuracy of n of course would be expected to become poor if x were not extended sufficiently high.

Although it is not obvious, the limit to the adsorption equation as x approaches 1.0 is the product of Bn. Since this is the product of the number of layers times the amount in each layer, such a result would be expected.

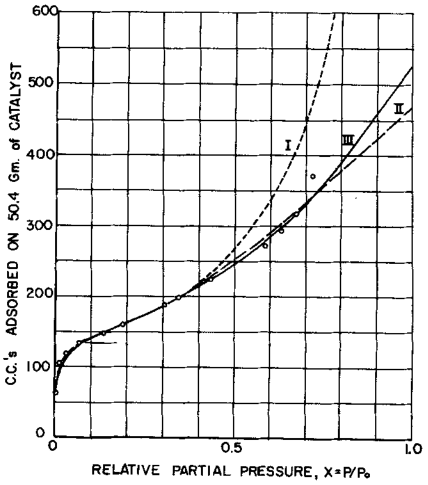

Fig. 3. Adsorption of nitrogen on iron aluminum oxide catalyst No. 954 at 932°F. (2) as correlated by B.E.T. equations (Curves I and II) and by the new equation (Curve III).

Application of Equation

The isotherm for the present equation was applied to well over two-hundred sets of adsorption data. The range of materials covered is given in Table 1. Most of the data are for the adsorption of water vapor on various hygroscopic materials; the variable x therefore represents the relative humidity in the surrounding atmosphere.

The standard deviation for both the adsorption and desorption data was 0.95 wt.%. This included twenty-eight sets of adsorption data by Bull (*16*) on proteins, many of which tended to form a solution at high humidities. Without the data of Bull the standard deviation dropped to 0.65 wt.%. For all of the materials tested the standard deviation was in the order of spread of the original data.

The type of fit obtained with data with little spread is illustrated by Figure 2. The numerical values of the constants B, C, and n for typical isotherms including the curves shown here are given in Table 2. Rough calculations show that cellulose data above 95% humidity should show capillary condensation to a measurable degree. Therefore data above 95% relative humidity were not included in these corrections. This is to imply that not only cellulose but all the materials will have pronounced capillary adsorption if the humidity is sufficiently high (22). This capillary adsorption is in addition to the adsorption described by the present equation.

The data presented by Brunauer, Emmett, and Teller in their paper (2) are plotted in Figure 3. In addition to the two curves evaluated by Brunauer et al. a third curve determined by the present equation is shown. The three curves shown are the best correlation by the following three equations:

1. The B.E.T. equation in its usual form

$$A = \frac{BCx}{[1 + (C-1)x]\,(1-x)} \tag{25}$$

2. The B.E.T. equation for finite number of layers

$$A = \frac{BCx}{(1-x)} \left[\frac{1 - (n+1)x^n + nx^{n+1}}{1 + (C-1)x \; - cx^{n+1}}\right] \tag{26}$$

3. The present equation.

Curve A rises too rapidly at higher pressures as the B.E.T. equation does for all materials. In its modified form the B.E.T. equation does not rise rapidly enough with pressure. The present equation appears to fit the data better with the notable exception of the highest point. Without this last point a nearly perfect correlation could be obtained. The rapid rise at this last point would seem to indicate capillary adsorption, although no proof can be offered for this assumption.

It is interesting to note that the value of B determined by the present equation was identical to that determined by Brunauer, Emmett, and Teller to the fourth figure.

As noted previously the values of the constants depend upon whether the vapor is being adsorbed or desorbed. The average value of B was found to be about 25% lower on adsorption than on desorption. This falls in line with the assumption that an impurity is adsorbed when the relative pressure is low, since the impurity would occupy adsorption sites and decrease the value of B in going from low to higher pressure. If a closed hysteresis loop is expected, then the product Bn must be the same for desorption as for adsorption. This was found to be approximately true for several samples of cellulose. In most cases however consistent curves were not obtained, since permanent changes take place in many materials during the initial cycles of adsorption desorption (*4*). A conditioning by exposure to alternate cycles of adsorption and desorption is necessary to stabilize the material.

Proper interpretation of the constant B is important. Although it represents the amount which corresponds to a monolayer, when this amount has been adsorbed the first layer is not complete; indeed the first layer is not completed until the partial pressure becomes saturated. This is illustrated by Figure 4, which shows the relative amount in each layer as the pressure is increased. Notice that molecules condense in small amounts in the upper layers even at low pressures. This probably occurs at the interstices of the material, where adsorption forces are unevenly distributed.

Scope of Use

Joyner, Weinberger, and Montgomery (*3*) have pointed out that the B.E.T. equation tends to give somewhat high adsorption values at very low humidities. The present equation will suffer this same fault.

Brunauer, Demming, Demming, and Teller (*26*) described a modification of the B.E.T. equation to account for filling of the capillary pore spaces and its attendant surface effects. Such an analysis may be applied to account for other possible isotherms. The sigmoid-shaped isotherms presented here are those most commonly encountered with water vapor.

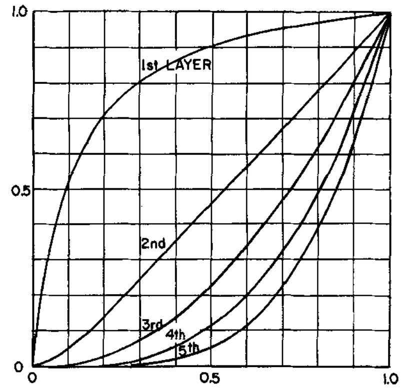

Fig. 4. Relative build-up of individual layers according to the new equation.

With proper attention to capillary condensation the present equation may be used to describe and extrapolate adsorption data for the range of relative vapor pressures met in practice.

NOTATION

A = amount of vapor adsorbed, lb. adsorbed/lb. adsorbent
A_0 = amount adsorbed in first layer per unit weight of adsorbent
B = amount adsorbed corresponding to a monolayer, lb. adsorbed/lb. adsorbent
C = partition function for adsorption energy including the configuration effects, $C = (j_1/j_l)\,e^{(E_a - E_l)/RT}$
E_a = energy of adsorption, B.t.u./lb. mole
E_l = energy of liquifraction of adsorbate, B.t.u./lb. mole
F = free energy (Gibbs)
i = subscript, layer number
I = intercept in Equation (20), equal to $1/BC$
j = configuration partition function
J = total partition function for layer, $J \equiv je^{E_a/RT}$
k = Boltzman constant; subscript, data number
n = number of layers
N = number of molecules adsorbed
N_0 = number of adsorption sites
P = pressure or partial pressure of vapor
P_0 = saturation pressure of vapor
Q = over-all partition function
R = perfect gas constant, B.t.u./lb. mole °R.
S = slope in Equation (20), equal to $(C - 1)/BC$
T = temperature
W = number of distinguishable configurations
x = relative partial pressure, equal to P/P_0
Y_c = B.E.T. variable to be correlated, equal to $x/[A(1-x)]$ $[A(1 - x)]$
Y_e = extrapolated value of Y_c
z = variable used in correlation, function of x
μ = chemical potential
μ_{og} = standard chemical potential of gas phase

LITERATURE CITED

1. Fowler, R., and E. A. Guggenheim, "Statistical Thermodynamics," Chap. 10, Cambridge Univ. Press, London (1939).
2. Brunauer, S., P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **69**, 309 (1938).
3. Joyner, L. G., E. B. Weinberger, and C. W. Montgomery, *ibid.*, **67**, 2183 (1936).
4. Simka, R., and J. W. Rowen, *ibid.*, **70**, 1663 (1948).
5. Ledoux, E., "Vapor Adsorption," pp. 25, 78, Chemical Publishing, New York (1945).
6. Cassie, A. B. D., *Trans. Faraday Soc.*, **41**, 450 (1945).
7. Sheppard, S. E., and P. T. Newsome, *Ind. Eng. Chem.*, **26**, 284 (1934).
8. Urquhart, R. A., and A. M. Williams, *J. Textile Instr., Trans.*, **15**, T 138 (1924).
9. Wahba, M., and S. Nashed, *ibid.*, **48**, T 1 (1947).
10. ———, and K. Aziz, *ibid.*, **49**, T 519 (1958).
11. Wiegerink, J. G., *Bur. Standards J. Research*, **24**, 645 (1940).
12. Hauser, P. M., and A. D. McLaren, *Ind. Eng. Chem.*, **40**, 112 (1949).
13. Simril, V. L., and S. Smith, *ibid.*, **34**, 226 (1942).
14. Jury, S. H., and William Licht, Jr., *Chem. Eng. Progr.*, **48**, 102 (1952).
15. Seborg, C. O., L. A. Simmonds, and P. K. Baird, *Ind. Eng. Chem.*, **28**, 1245 (1936).
16. Bull, H. B., *J. Am. Chem. Soc.*, **66**, 1499 (1944).
17. Kessler, C. C., J. E. Killinger, and E. T. Kjermstad, *Paper Trade J.*, **TAPPI Section**, 122, 133 (1948).
18. Mellon, E. F., A. H. Korn, and S. R. Hoover, *J. Am. Chem. Soc.*, **69**, 827 (1947).
19. Campbell, R., *Paper Trade J.*, **73**, No. 2, 30 (1921).
20. "International Critical Tables," Vol. 2, pp. 322-325, McGraw-Hill, New York (1928).
21. Seborg, C. O., and A. J. Stamm, *Ind. Eng. Chem.*, **23**, 1271 (1931).
22. Van den Akker, J. A., W. A. Wink, and F. C. Bobb, *TAPPI*, **42**, 340 (1959).
23. Wink, W. A., F. C. Bobb, and J. A. Van den Akker, *ibid.*, **41**, 643 (1958).
24. Taylor, R. K., *Ind. Eng. Chem.*, **37**, 649 (1945).
25. Cassie, A. B. D., *Trans. Faraday Soc.*, **41**, 458 (1945).
26. Brunauer, S., L. S. Demming, E. W. Demming, and E. Teller, *J. Am. Chem. Soc.*, **62**, 1723 (1940).

Manuscript received February 19, 1960; revision received August 22, 1960; paper accepted September 1, 1960. Paper presented at A.I.Ch.E. Washington meeting.