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Theory of Multimolecular Adsorption from a Mixture of Gases

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By making use of the evaporation-condensation properties of liquid mixtures, the Brunauer-Emmett-Teller theory of multimolecular adsorption is extended to mixtures of gases. No satisfactory experimental data are available at the present time with which to test the theory.

INTRODUCTION

PERHAPS the most important postulate in the Brunauer-Emmett-Teller[1] (BET) theory of multimolecular adsorption is that molecules of the second and higher adsorbed layers have the evaporation-condensation properties of the liquid state. If this postulate has really general validity (as a good approximation), one should be able to treat adsorption from a mixture of gases by assuming that molecules of the second and higher adsorbed layers in this more complicated case have the evaporation-condensation properties of a liquid mixture at the same temperature and composition. Hence, a comparison between experiment and a theory based on this assumption would provide a further test of the fundamental ideas underlying the BET treatment. Such a theory is developed in this paper[2a] but, unfortunately, satisfactory experimental data for comparison are apparently not yet available.

ADSORPTION FROM A MIXTURE OF TWO GASES

We shall be interested in the adsorption of two gases A and B at relative pressures $x_A = p_A/p_A{}^0$ and $x_B = p_B/p_B{}^0$, and at a temperature T below both critical temperatures. Let q_A, q_B, q_{AA}, q_{BB}, q_{AB}, q_{BA}, q_{AN_A}, and q_{BN_A} be, respectively, the heats of adsorption per mole of A on the bare surface of the solid, B on the bare surface, A on a layer of pure A, B on a layer of pure B, A on a layer of pure B, B on a layer of pure A, A on a layer of composition N_A (mole fraction of A), and B on a layer of composition N_A.

We consider various evaporation-condensation equilibria. First, if we have pure liquid A (or B)

of surface area s in equilibrium with its vapor, then

$$\begin{cases} a_A s p_A{}^0 = b_A s \exp(-q_{AA}/RT), \\ a_B s p_B{}^0 = b_B s \exp(-q_{BB}/RT), \end{cases} \quad (1)$$

or

$$\frac{b_A}{a_A} = p_A{}^0 \exp(q_{AA}/RT),$$
$$\frac{b_B}{a_B} = p_B{}^0 \exp(q_{BB}/RT). \quad (2)$$

Next, if a binary liquid mixture of composition N_A is in equilibrium with its vapor, we have

$$\begin{cases} a_A s p_A = b_A s N_A \exp(-q_{AN_A}/RT), \\ a_B s p_B = b_B s (1-N_A) \exp(-q_{BN_A}/RT). \end{cases} \quad (3)$$

On substituting Eqs. (2) into (3), one obtains

$$\begin{cases} p_A/p_A{}^0 = x_A = N_A \exp[(q_{AA}-q_{AN_A})/RT], \\ p_B/p_B{}^0 = x_B = (1-N_A) \\ \qquad\qquad \times \exp[(q_{BB}-q_{BN_A})/RT]. \end{cases} \quad (4)$$

In studying below the equilibria involved in adsorption, it will be necessary to have $(q_{AA}-q_{AN_A})$ and $(q_{BB}-q_{BN_A})$ as functions of N_A. The nature of the dependence of these quantities on N_A may be found from the experimental vapor pressure curves, which can be expressed in the form

$$\begin{cases} x_A = N_A/f_A(N_A), \qquad f_A(N_A) = N_A/x_A, \\ x_B = (1-N_A)/f_B(N_A), \quad f_B(N_A) = (1-N_A)/x_B. \end{cases} \quad (5)$$

That is, the functions $f_A(N_A)$ and $f_B(N_A)$ may be tabulated from the experimental values of x_A, x_B, and N_A. Comparing Eqs. (4) and (5):

$$\begin{cases} \exp[(q_{AN_A}-q_{AA})/RT] = f_A(N_A), \\ \exp[(q_{BN_A}-q_{BB})/RT] = f_B(N_A). \end{cases} \quad (6)$$

We turn now to adsorption equilibria. In addition to the postulates of the BET theory,

[1] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc., **60**, 309 (1938).
[2a] See also T. L. Hill, J. Chem. Phys., **14**, 46 (1946).

we make a further assumption:[2b] the average energy of attachment of a molecule on top of the $(i-1)$th layer (to become a member of the ith layer) depends on the composition of the $(i-1)$th layer only. Let s_i represent the surface area covered by exactly i layers of adsorbed molecules and let N_{Ai} be the composition of the ith layer. Then, when equilibrium is established between all of the layers, we will have

$$\begin{cases} a_A s_0 p_A = b_A s_1 N_{A1} \exp(-q_A/RT), \\ a_B s_0 p_B = b_B s_1 (1-N_{A1}) \exp(-q_B/RT), \end{cases} \quad (7)$$

$$i=2,3,\cdots \begin{cases} a_A s_{i-1} p_A = b_A s_i N_{Ai} \\ \qquad \times \exp(-q_A N_{A(i-1)}/RT), \\ a_B s_{i-1} p_B = b_B s_i (1-N_{Ai}) \\ \qquad \times \exp(-q_B N_{A(i-1)}/RT). \end{cases}$$

If we use Eqs. (2) and (6) in Eqs. (7), we can write

$$\begin{cases} s_1 N_{A1} = s_0 x_A Q_A, \\ s_1(1-N_{A1}) = s_0 x_B Q_B, \end{cases}$$

$$i=2,3,\cdots \begin{cases} s_i N_{Ai} = s_{i-1} x_A f_A(N_{A i-1}), \\ s_i(1-N_{Ai}) = s_{i-1} x_B f_B(N_{A i-1}), \end{cases} \quad (8)$$

where

$$\begin{cases} Q_A = \exp[(q_A - q_{AA})/RT], \\ Q_B = \exp[(q_B - q_{BB})/RT]. \end{cases} \quad (9)$$

By combining Eqs. (8) in an appropriate manner, there results

$$s_i = s_{i-1} E_{i-1} = s_0 E_0 E_1 E_2 \cdots E_{i-1},$$
$$i=1, 2, \cdots \quad (10)$$

$$\begin{cases} E_0 = x_A Q_A + x_B Q_B, \\ E_i = x_A f_A(N_{Ai}) + x_B f_B(N_{Ai}), \end{cases} \quad (11)$$
$$i=1, 2, \cdots$$

$$\begin{cases} N_{A1} = x_A Q_A/E_0, \\ N_{Ai} = x_A f_A(N_{A i-1})/E_{i-1}, \quad i=2, 3, \cdots. \end{cases} \quad (12)$$

Let v_A and $v_m{}^A$ be the volume of A adsorbed and the volume of A necessary to give a complete unimolecular layer, respectively. Then, as in the BET theory, we can relate $v_A/v_m{}^A$ to the areas $s_0, s_1, s_2, \cdots$. If γ_{Ai} is the fraction of the area of the ith layer $(s_i + s_{i+1} + \cdots)$ which is made up of A molecules, we have

$$\frac{v_A}{v_m{}^A} = \frac{(s_1 + s_2 + \cdots + s_n)\gamma_{A1} + (s_2 + \cdots + s_n)\gamma_{A2} + \cdots + s_n \gamma_{An}}{s_0 + s_1 + \cdots + s_n}. \quad (13)$$

In writing Eq. (13), the number of layers is restricted to n. The case of most interest is $n = \infty$. Substituting Eq. (10) into Eq. (13) gives

$$\frac{v_A}{v_m{}^A} = \frac{E_0[(1 + E_1 + E_1 E_2 + \cdots + E_1 E_2 \cdots E_{n-1})\gamma_{A1} + (E_1 + \cdots + E_1 E_2 \cdots E_{n-1})\gamma_{A2} + \cdots + E_1 \cdots E_{n-1}\gamma_{An}]}{1 + E_0(1 + E_1 + E_1 E_2 + \cdots + E_1 E_2 \cdots E_{n-1})}. \quad (14)$$

We assume that the area fraction γ_A is related to the mole fraction N_{A1} to a sufficient approximation, by

$$\gamma_A = \frac{N_A}{N_A + (1-N_A)(v_B{}^0/v_A{}^0)^{\frac{1}{3}}}, \quad (15)$$

where $v_A{}^0$ and $v_B{}^0$ are molar volumes. In ordinary cases, the error made by replacing the γ_{Ai} in Eq. (14) by the N_{Ai} is not serious. For example, if $v_A{}^0$ and $v_B{}^0$ differ by 20 percent, γ_A and N_A differ on the average (from $N_A = 0$ to $N_A = 1$) by

about 5 percent. In a more exact treatment of any given case, a curve of γ_A against N_A should be plotted for the appropriate $v_B{}^0/v_A{}^0$. Then, in using Eq. (14), γ_{Ai} may be read from the curve, for each N_{Ai} obtained from Eq. (12).

The quantity $v_B/v_m{}^B$ may be obtained from Eq. (14) by replacing the γ_{Ai} by $1 - \gamma_{Ai}$.

If $E_\infty \geqslant 1$, Eq. (14) does not converge for $n = \infty$: $v_A/v_m{}^A$ and $v_B/v_m{}^B$ become infinite. This corresponds physically to condensation on the surface of the adsorbent. The value of E_∞ may be obtained easily from

$$N_{A\infty} = \frac{x_A f_A(N_{A\infty})}{x_A f_A(N_{A\infty}) + x_B f_B(N_{A\infty})}, \quad (16)$$

$$E_\infty = x_A f_A(N_{A\infty}) + x_B f_B(N_{A\infty}). \quad (17)$$

[2b] It will be seen from the statistical mechanical discussion of the BET theory in the accompanying paper that this assumption is the most natural one to make for this model. In fact, from the point of view of this statistical treatment (where only vertical interactions are taken into account), no new postulate is really necessary. That is, the assumption under discussion follows from the BET model.

It will be noted that N_{A_∞} and E_∞ are independent of the nature (Q_A and Q_B) of the surface of the adsorbent. The influence of the surface dies out as the number of layers increases. As one should expect, if we put $E=1$ (condensation) in Eqs. (16) and (17), we obtain the vapor pressure equations, Eqs. (5).

There is no difficulty in applying these equations when liquid A and B are immiscible over part or all of the range in N_A. The experimental vapor pressure curves are used as in other cases.

If $x_B=0$ (or $x_A=0$), Eq. (14) reduces to the usual BET equation with $\gamma_{A_i}=N_{A_i}=1$, $E_i=x_A=x$, and $E_0=x_AQ_A=xc$. A similar result is obtained in the very special case: $E_1=E_2=E_3=\cdots=E$ and $N_{A_1}=N_{A_2}=N_{A_3}=\cdots=N_A$. In this event,

$$\frac{v_A}{v_m^A}=\frac{E_0N_A}{(1-E)(1-E+E_0)}. \qquad (17a)$$

ADSORPTION FROM A MIXTURE OF MORE THAN TWO GASES

Suppose we have a mixture of gases A, B, C, $\cdots$. We retain the same symbols as above except that we use q_{AN}, $f_A(N)$, etc., in which N represents the composition (N_A, N_B, N_C, $\cdots$). The extension of Eqs. (3) to (17) to this more general case is obvious. In particular, Eqs. (10), (13), and (14) are unchanged and Eqs. (11), (12), and (15) become, respectively,

$$\begin{cases} E_0=x_AQ_A+x_BQ_B+x_CQ_C+\cdots, \\ E_i=x_Af_A(N_i)+x_Bf_B(N_i) \\ \qquad +x_Cf_C(N_i)+\cdots, \quad i=1, 2, \cdots \end{cases} \qquad (18)$$

$$\begin{cases} N_{A_1}=x_AQ_A/E_0, \\ N_{A_i}=x_Af_A(N_{i-1})/E_{i-1}, \quad i=2, 3, \cdots \end{cases} \qquad (19)$$

$$\gamma_A=\frac{N_A}{N_A+N_B(v_B^0/v_A^0)^{\frac{3}{2}}+N_C(v_C^0/v_A^0)^{\frac{3}{2}}+\cdots}. \qquad (20)$$

In order to use Eq. (20) in Eq. (14), it is clear that the N_{B_i}, N_{C_i}, etc., must also be computed as in Eq. (19). However, $\gamma_{A_i}=N_{A_i}$ will still be a fairly good approximation in most cases.

APPROXIMATIONS

Vapor Pressure Curves

If the vapor pressure curves of A and B show the usual Henry's law and Raoult's law char-

acteristics at small and large mole fractions, respectively, it may prove convenient to represent the experimental vapor pressure curves by simple analytical expressions and use these in place of $f_A(N_A)$ and $f_B(N_A)$. Suitable equations for this purpose are[3]

$$x_A=N_A/Q_{AB}{}^\beta, \qquad \beta=(1-N_A)^2$$
$$x_B=(1-N_A)/Q_{BA}{}^\alpha, \quad \alpha=N_A{}^2 \qquad (21)$$

with

$$Q_{AB}=\exp[(q_{AB}-q_{AA})/RT],$$
$$Q_{BA}=\exp[(q_{BA}-q_{BB})/RT]. \qquad (22)$$

The connection between w_{AB} of Fowler and Guggenheim[3] and our symbols is

$$\exp(-2w_{AB}/kT)=Q_{AB}Q_{BA}=Q^2. \qquad (23)$$

If $Q=1$, the solution is ideal and Raoult's law is obeyed over the whole range of composition. If $Q>1$, A and B attract each other more than do like molecules, hence x_A and x_B are less than N_A and $1-N_A$, respectively. If $Q<1$, the situation is reversed. If $Q\leqslant 1/e^2=0.135$, two phases exist over part of the range in composition and Eqs. (21) can no longer be used as satisfactory approximations to the true state of affairs.

In this approximation

$$f_A(N_A)=Q_{AB}{}^\beta, \quad f_B(N_A)=Q_{BA}{}^\alpha. \qquad (24)$$

Hence, from Eqs. (11) and (12),

$$E_i=x_AQ_{AB}{}^{\beta(i)}+x_BQ_{BA}{}^{\alpha(i)}, \quad i=1, 2, \cdots \qquad (25)$$

$$N_{A_i}=x_AQ_{AB}{}^{\beta(i-1)}/E_{i-1}, \quad i=2, 3, \cdots. \qquad (26)$$

For more than two gases,

$$E_i=x_AQ_{AB}{}^{\varphi(B)}Q_{AC}{}^{\varphi(C)}\cdots$$
$$\qquad +x_BQ_{BA}{}^{\varphi(A)}Q_{BC}{}^{\varphi(C)}\cdots+\cdots, \qquad (27)$$

etc., with

$$\varphi(A)=N_{A_i}{}^2, \quad \varphi(B)=N_{B_i}{}^2, \quad \text{etc.}$$

[3] See, for example, R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 357. By not necessarily requiring, in Eqs. (21), that $Q_{AB}=Q_{BA}$, it is possible in some cases to fit the experimental data better (if $Q_{AB}=Q_{BA}$, the curves for x_A and x_B are required to be identical except for inversion). This practical advantage is at the expense of thermodynamics, however, since Eqs. (21) satisfy

$$N_A\frac{\partial \log x_A}{\partial N_A}=N_B\frac{\partial \log x_B}{\partial N_B}$$

only if $Q_{AB}=Q_{BA}$. This suggests the policy of using Eqs. (21) only when a satisfactory fit may be obtained with $Q_{AB}=Q_{BA}$, and employing the experimental vapor pressure curves otherwise. If this policy is adopted, read $Q_{AB}=Q_{BA}$ throughout the paper.

Approximations of Eq. (14)

In addition to approximating the experimental vapor pressure curves, it is highly desirable to have approximate forms of Eq. (14). It should be emphasized that the approximate equations given below are in the nature of suggestions only, based, however, on the calculation of a number of widely different cases (using Eq. (24)). It is possible that a more complete study would lead to significant improvements.

The sequences N_{A1}, N_{A2}, N_{A3}, $\cdots$ and E_1, E_2, E_3, $\cdots$ approach limits $N_{A\infty}$ and E_∞, respectively, given by Eqs. (16) and (17). In most cases studied, successive values of N_{Ai} oscillate above and below $N_{A\infty}$, with steadily decreasing amplitude, while the E_i do not show such oscillations.[4] In all cases studied, the E_i converge much more rapidly than the N_{Ai}.

The method of approximation used is to break off the sums in Eq. (14) at a certain value of i, and use mean values to obtain closed expressions representing the rest of the sum. For example,

$$1+E_1+E_1E_2+E_1E_2E_3+\cdots$$
$$\cong 1+E_1+E_1E_2(1+E+E^2+\cdots)$$
$$\cong 1+E_1+E_1E_2/(1-E), \quad (28)$$

where E is some mean value, say, $(E_3E_\infty)^{\frac{1}{2}}$.

On the basis of an incomplete study, the following scheme is suggested (for $n=\infty$) in order to obtain approximate values which differ from those given by Eq. (14) by less than about 3 percent:

I. If E_1 differs from E_2 by less than 4 percent:

$$X=\left(\gamma_{A1}+\frac{E\gamma_A}{1-E}\right)\frac{1}{1-E}, \quad (29)$$

with
$$Y=1/(1-E) \quad (30)$$
$$E=E_\infty \quad \text{and} \quad \gamma_A=\gamma_{A\infty}. \quad (31)$$

II. If E_1 differs from E_2 by from 4 percent to about 50 percent:

$$X=\gamma_{A1}+\left(\gamma_{A1}+\gamma_{A2}+\frac{E\gamma_A}{1-E}\right)\frac{E_1}{1-E}, \quad (32)$$

$$Y=1+E_1/(1-E), \quad (33)$$

with $E=(E_2E_\infty)^{\frac{1}{2}}$ and

$$\begin{aligned}\gamma_A&=\gamma_{A\infty}(\text{osc.})\\&=(\gamma_{A3}\gamma_{A\infty})^{\frac{1}{2}}(\text{non-osc.}).\end{aligned} \quad (34)$$

III. If E_1 differs from E_2 by more than about 50 percent:

$$X=\gamma_{A1}+(\gamma_{A1}+\gamma_{A2})E_1$$
$$+\left(\gamma_{A1}+\gamma_{A2}+\gamma_{A3}+\frac{E\gamma_A}{1-E}\right)\frac{E_1E_2}{1-E}, \quad (35)$$

$$Y=1+E_1+E_1E_2/(1-E) \quad (36)$$

with $E=(E_3E_\infty)^{\frac{1}{2}}$ and

$$\begin{aligned}\gamma_A&=\gamma_{A\infty}(\text{osc.})\\&=(\gamma_{A4}\gamma_{A\infty})^{\frac{1}{2}}(\text{non-osc.}).\end{aligned} \quad (37)$$

In the above equations, $n=\infty$, and

$$\frac{v_A}{v_m{}^A}=\frac{E_0X}{1+E_0Y}. \quad (38)$$

The mean values suggested are, of course, rather arbitrary, but have some justification. Values of γ_A are obtained from the corresponding values of N_A, using Eq. (15). In Eqs. (34) and (37), where two values of γ_A are given, the first is to be used if the N_{Ai} exhibit oscillations of the type discussed above. Otherwise, the second value is to be used.

For finite values of n, Eq. (14) itself is only a rough approximation since capillary condensation is neglected. Also, approximate equations of the type given above become rather complicated. Hence, it is probably not worth while to use approximate equations for finite values of n except, perhaps, in case I above. The complete Eq. (14) is almost as easy to use in cases II and III. For case I, one finds

$$\frac{v_A}{v_m{}^A}=\frac{E_0\{\gamma_{A1}(E^{n+1}-E^n-E+1)+\gamma_A[(n-1)E^{n+1}-nE^n+E]\}}{(1-E)[1-E-E_0(E^n-1)]}, \quad (39)$$

with
$$E=E_\infty \quad \text{and} \quad \gamma_A=\gamma_{A\infty}.$$

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[4] Oscillations of this type in E_i are, in fact, not possible. For it is not difficult to show, using the thermodynamic equation in footnote 3, that $E(N_A)$ has a maximum ($Q<1$) or a minimum ($Q>1$) at that value of N_A which satisfies Eq. (16). That is, E_∞ is the largest or smallest possible value of E and $N_{A\infty}$ is the associated value of N_A.
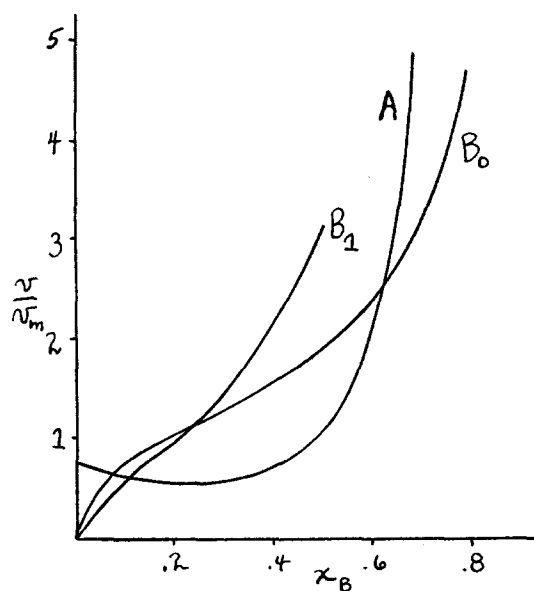
FIG. 1.

Since Eq. (14) holds regardless of the number of gases in the mixture, the above approximations to this equation should have essentially the same validity in the general problem of any number of gases as they have in the special case of a mixture of two gases.

EXAMPLE

As far as the author is aware, no experimental data are available at the present time which can be used to test the theory properly. The following experimental results are desirable: (1) vapor pressure curves for A and B as functions of N_A; (2) adsorption isotherms (at the same temperature as in the vapor pressure experiments) for

pure A and pure B, preferably on a non-porous adsorbent (to reduce complications); (3) adsorption isotherms (at the same temperature and on the same adsorbent) of A and B from mixtures of gases. Curves of $v_A/v_m{}^A$ and $v_B/v_m{}^B$ should be obtained as functions of, say, x_A for a series of values of x_B. The vapor pressure curves give $f_A(N_A)$ and $f_B(N_A)$ (or Q) while the adsorption isotherms for pure A and pure B can be used to obtain Q_A, Q_B, $v_m{}^A$, and $v_m{}^B$. Then the theoretical isotherms for mixtures of A and B may be calculated and compared with experiment. For more than two gases, the vapor pressures can be studied in pairs, as implied in Eq. (27).

In order to illustrate certain features predicted by theory, we have plotted in Fig. 1 isotherms for a hypothetical case (using Eq. (24), $v_A{}^0 = v_B{}^0$ and $n = \infty$). We have chosen a fairly typical case: $Q = 4$, $Q_A = Q_B = Q' = 20$. In this figure, curve B_0 gives $v_B/v_m{}^B$ as a function of x_B for $x_A = 0$. Curve B_1 shows the effect of a constant pressure of A: $v_B/v_m{}^B$ is plotted against x_B for $x_A = .1$. At the lower pressures of B, the presence of A inhibits the adsorption of B, but this effect is reversed at higher pressures. Curve A of Fig. 1 represents the adsorption of A as a function of x_B for constant $x_A = .1$. The adsorption of A at constant pressures of A is reduced by the presence of small amounts of B but greatly increased for sufficiently large pressures of B. These effects are due to Q' being considerably larger than Q. A and B compete for positions in the first layer and the molecules of the first layer do not attract additional molecules to the extent that the bare surface does. Hence, at low pressures, the competition reduces adsorption of both A and B.

CAPILLARY CONDENSATION

It has been recognized that capillary condensation cannot be treated satisfactorily by merely assigning an appropriate finite value to n in the original[1] BET theory. In a later paper,[5] Brunauer, Deming, Deming, and Teller improved the theory by taking into account the additional energy of adsorption in the last adsorbed layer. More recently, Pickett[6] has introduced a modification of the BET theory which appears to be an empirical improvement (for n finite) but which lacks theoretical justification (in the opinion of the present writer[7]).

Before considering mixtures, several corrections to the capillary condensation equations[5] of the BET theory will be suggested. For simplicity we shall not consider the most general of these equa-

[5] S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, J. Am. Chem. Soc. **62**, 1723 (1940).
[6] G. Pickett, J. Am. Chem. Soc. **67**, 1958 (1945).
[7] T. L. Hill, J. Am. Chem. Soc. **68**, 535 (1946).

tions (Eq. (E)) but the same argument holds. Eq. (D) is derived from

$$\frac{v}{v_m} = \frac{2[s_1 + 2s_2 + \cdots + (n-1)s_{n-1}] + ns_n}{2(s_0 + s_1 + \cdots + s_{n-1}) + s_n} \tag{40}$$

for the case of $2n-1$ layers fitting into a capillary. It appears to the writer that the contribution of s_n to both numerator and denominator has been handled incorrectly and Eq. (40) should read

$$\frac{v}{v_m} = \frac{2[s_1 + 2s_2 + \cdots + (n-1)s_{n-1}] + (2n-1)s_n}{2(s_0 + s_1 + \cdots + s_n)}. \tag{41}$$

This gives

$$\frac{v}{v_m} = \frac{cx\left[1 + \left(\frac{2n-1}{2}g - n\right)x^{n-1} - (2ng - g - n + 1)x^n + \frac{2n-1}{2}gx^{n+1}\right]}{(1-x)[1 + (c-1)x + (cg-c)x^n - cgx^{n+1}]} \tag{42}$$

instead of Eq. (D). For the case of $2n$ layers fitting into a capillary, similar reasoning leads to

$$\frac{v}{v_m} = \frac{2(s_1 + 2s_2 + \cdots + ns_n)}{2(s_0 + s_1 + \cdots + s_n)} \tag{43}$$

$$= \frac{cx[1 + (ng-n)x^{n-1} - (2ng - n + 1)x^n + ngx^{n+1}]}{(1-x)[1 + (c-1)x + (cg-c)x^n - cgx^{n+1}]}. \tag{44}$$

Using the principle of Pickett's modification, one finds, instead of Eqs. (42) and (44),

$$\frac{v}{v_m} = \frac{cx\left[1 + \left(\frac{2n-1}{2}g - n\right)x^{n-1} + \left(n - 1 - \frac{2n-1}{2}g\right)x^n\right]}{(1-x)\{1 - x + c[x^n(g-1) + x]\}}, \tag{45}$$

and

$$\frac{v}{v_m} = \frac{cx[1 + (ng-n)x^{n-1} + (n-1-ng)x^n]}{(1-x)\{1 - x + c[x^n(g-1) + x]\}}. \tag{46}$$

Eq. (46) is thus a correction to Pickett's Eq. (8).

In dealing with a mixture of gases (say, two, for example), Eqs. (8) remain unchanged except for $i = n$:

$$\begin{cases} s_n N_{An} = s_{n-1}x_A f_A(N_{An-1})g_A, \\ s_n(1 - N_{An}) = s_{n-1}x_B f_B(N_{An-1})g_B, \end{cases} \tag{47}$$

where $g = \exp(\epsilon/RT)$ as in reference 5 (ϵ replacing Q). The quantities ϵ_A and ϵ_B will depend here on the composition of the $(n-1)$th layer. The E_i and N_{Ai} are unchanged except for $i = n-1$ and $i = n$, respectively. In these cases we write

$$\mathcal{E}_{n-1} = x_A g_A f_A(N_{An-1}) + x_B g_B f_B(N_{An-1}), \tag{48}$$

and

$$\mathcal{N}_{An} = x_A g_A f_A(N_{An-1})/\mathcal{E}_{n-1}. \tag{49}$$

Eq. (10) holds except for $i = n$:

$$s_n = s_{n-1}\mathcal{E}_{n-1}. \tag{50}$$

Then, for $2n-1$ layers fitting into a capillary,

$$\frac{v_A}{v_m{}^A} = \frac{2[(s_1 + s_2 + \cdots + s_n)\gamma_{A1} + (s_2 + \cdots + s_n)\gamma_{A2} + \cdots + (s_{n-1} + s_n)\gamma_{An-1}] + s_n\gamma_{An}}{2(s_0 + s_1 + \cdots + s_n)}, \tag{51}$$

where s_n is obtained from Eq. (50) and γ_{An} is given by Eq. (15) using $\mathcal{N}_{An}$. For $2n$ layers fitting into a capillary, the two factors of 2 in Eq. (51) should be omitted.

Using Pickett's modification,

$$\mathcal{E}_{n-1} = \frac{x_A g_A f_A (N_{A_{n-1}})}{1 - x_A} + \frac{x_B g_B f_B (N_{A_{n-1}})}{1 - x_B} \tag{52}$$

and

$$\mathfrak{N}_{A_n} = \frac{x_A g_A f_A (N_{A_{n-1}})}{(1 - x_A) \mathcal{E}_{n-1}}. \tag{53}$$

The next problem is the evaluation of the g's. We can write[5]

$$\epsilon_A = 2k_A S_A \sigma_{N_{A(n-1)}}, \quad \epsilon_B = 2k_B S_B \sigma_{N_{A(n-1)}}, \tag{54}$$

where $\sigma_{N_{A(n-1)}}$ is the surface tension of a solution of A and B of composition $N_{A_{n-1}}$, and S_A and S_B are the surface areas covered by one mole of A and B, respectively, spread out into a unimolecular layer. As an approximation, the constants k_A and k_B may be taken as equal to each other. Then,

$$\frac{\epsilon_A}{\epsilon_B} = \frac{S_A}{S_B} = \frac{V_A^{\frac{2}{3}}}{V_B^{\frac{2}{3}}}, \tag{55}$$

where V_A and V_B are molar volumes. This equation can be used to reduce the number of parameters by one, since it gives a relation between g_A and g_B. A further approximation is to assume $k_A = k_B = 1$ and a particular type of packing. If the surface tensions of A and B are known, and a linear relationship[8] between surface tension and composition assumed (or the actual relationship measured), then g_A and g_B may be calculated using Eqs. (54).

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APPENDIX

In this section two miscellaneous points which may be of interest will be mentioned briefly.

1. The logic used by Brunauer, Emmett, and Teller[1] in deriving the equation

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \tag{56}$$

can be improved a little. After obtaining the equation

$$\frac{v}{v_m} = c \sum_{i=1}^{\infty} i x^i \bigg/ 1 + c \sum_{i=1}^{\infty} x^i, \tag{57}$$

it is really not legitimate to rewrite the sums in closed form (as is done in reference 1) without first making clear that values of x greater than unity have no physical significance (at this point in the derivation we know only that x is proportional to p). After writing Eq. (57), the next step should be either: (1) use the equations (in the BET notation)

$$x = (a/b)p \exp(E_L/RT), \tag{58}$$

and

$$asp^0 = bs \exp(-E_L/RT), \tag{59}$$

to obtain

$$x = p/p^0, \tag{60}$$

where Eq. (59) is the same as Eq. (1); or (2) point out that in Eq. (57) v is finite for $x < 1$ and infinite for $x \geqslant 1$ and furthermore that we desire v to be finite for $p < p^0$ and to be infinite for $p \geqslant p^0$, hence $x = 1$ should be identified with $p = p^0$. One may then proceed from Eq. (57) to Eq. (56).

2. In the usual BET theory with $n = \infty$, it is instructive to have some idea of the extent to which

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[8] N. A. Yajnik, R. K. Sharma, and M. C. Bharadway, J. Indian Chem. Soc. **3**, 63 (1926).

the surface of the adsorbent is covered as a function of v/v_m and c. If we use

$$1-\frac{s_0}{A}=\frac{cx}{1-x+cx}=\frac{v}{v_m}(1-x),\tag{61}$$

and Eq. (56) (to give x as a function of v/v_m), we find

$$1-\frac{s_0}{A}=\frac{c\left(\frac{v}{v_m}+1\right)-\left[\left(1-\frac{v}{v_m}\right)^2c^2+4\frac{v}{v_m}c\right]^{\frac{1}{2}}}{2(c-1)}\tag{62}$$

as the desired expression relating the fraction of the surface covered to c and v/v_m. For $v/v_m=1$,

$$1-\frac{s_0}{A}=\frac{c-(c)^{\frac{1}{2}}}{c-1},\tag{63}$$

and for $v/v_m=2$,

$$1-\frac{s_0}{A}=\frac{3c-(c^2+8c)^{\frac{1}{2}}}{2(c-1)}.\tag{64}$$

Some values of $1-(s_0/A)$ are given in Table I for these two cases. It is fairly customary to view the process of adsorption, as the pressure is gradually increased from $p=0$, as taking place essentially in the following manner: first, the first layer is laid down and then, at about $v=v_m$, the second layer begins to fill in, etc. It should be clear from Table I that, according to the BET theory, this picture of the process is satisfactory for large values of c, but not otherwise. For very small values of c, most of the adsorption when $v/v_m=1$ takes place primarily by attaching to molecules already adsorbed rather than by attaching to the bare surface. For example, for $c=.01$, when sufficient molecules have been adsorbed to cover the entire surface with a unimolecular layer $(v=v_m)$, actually only about one-tenth of the surface is covered. Hence, that part of the surface which is covered has, on the average, adsorbed molecules about ten layers thick.

TABLE I.

c	$v/v_m=1$	$v/v_m=2$
		$1-(s_0/A)$	
.001	.031	.043
.01	.091	.128
.1	.240	.333
1.	.500	.667
10.	.760	.921
100.	.909	.990
1000.	.969	.999