# Statistical Mechanics of Multimolecular Adsorption. IV. The Statistical Analog of the BET Constant a1b2/b1a2. Hindered Rotation of a Symmetrical Diatomic Molecule Near a Surface

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# Statistical Mechanics of Multimolecular Adsorption. IV. The Statistical Analog of the BET Constant $a_1b_2/b_1a_2$. Hindered Rotation of a Symmetrical Diatomic Molecule Near a Surface

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An approximate study is made of the restricted rotation of a symmetrical diatomic molecule near a surface. This makes possible some calculations concerning the BET constant $C = R \exp(\epsilon_1 - \Lambda)/kT$, and especially the factor $R$ (which is customarily set equal to unity). Cassie has pointed out that if this factor is set equal not to unity but to about 1/50 or even less, the low values of the heat of adsorption usually found on putting $R=1$ in the analysis of data are accounted for. The results obtained here indicate, unfortunately, that this factor is of the order of, say, 5–10, and that another explanation of the low heats of adsorption mentioned above will have to be found. An alternative method of estimating the area occupied per molecule in a completely filled monolayer is mentioned in an appendix.

The temperature dependence of the quantity $R$ is of some experimental interest, and a brief discussion of this dependence as predicted by the present approximate treatment is included.

## I. INTRODUCTION

WE are presenting in this series of papers[1–3] an approximate statistical theory of multimolecular adsorption. Statistical analogs of the BET constant $C$ have appeared, expressed in terms of the energy of adsorption, the partition function and energy of molecules in the liquid state, the partition function of molecules in the gas phase, and the partition function of molecules in the first adsorbed layer.[4] There are available useful theoretical studies concerning all of these quantities except the last. Except for the very simplest cases, a really refined study of the degrees of freedom (and hence of the partition function) of molecules physically adsorbed on a surface seems out of the question at present because of mathematical difficulties. (The way to proceed in principle is quite clear.) The point of view of the present paper, therefore, is to try to get semiquantitative results which will be helpful at least in giving a general understanding of the essential features involved. As a start, we confine ourselves here, for the most part, to the adsorption of symmetrical diatomic molecules. Even for this case, as will be seen below, some fairly rough approximations are made in order to avoid excessive complications. We hope to consider more complicated molecules at a later time. One incidental question of interest in this connection is the extent to which a large molecule, for example, n-heptane, actually "lies flat" on a surface, and how this property varies with the temperature.

### Degrees of Freedom

The three translational degrees of freedom of a monatomic molecule in the gas phase become (usually) two translational degrees (motion parallel to the surface) and one vibrational degree (motion perpendicular to the surface) on physical adsorption. In extreme cases (very low temperatures) the two translational degrees above may become[2] vibrational degrees.

The three translational, two rotational, and one internal vibrational degrees of freedom of a symmetrical diatomic molecule become, on physical adsorption, two translational, two rotational, one internal vibrational, and one vibrational degree (center of mass) perpendicular to the surface. However, the rotational motion will be seriously altered by the surface, the surface essentially introducing a potential barrier restricting the turning over of the molecule. In the extreme case of a very high barrier or low temperature the two rotational degrees will become effectively one degree of planar rotation (rotation of the mole-

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[1] T. L. Hill, J. Chem. Phys. **14**, 263 (1946).
[2] T. L. Hill, J. Chem. Phys. **14**, 441 (1946).
[3] T. L. Hill, J. Chem. Phys. **15**, 767 (1947).
[4] A more refined theory must, of course, not assume that molecules in all layers save the first have liquid-like properties.

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cule about an axis perpendicular to the surface, the molecular axis being parallel to the surface) and one degree of vibration (rocking of the molecular axis out of a plane parallel to the surface). The internal vibrational degree will, of course, also be perturbed by the surface, but much less strongly. This is because the forces introduced by the surface are generally rather small compared to the restoring force involved in the internal vibration.[5]

## Model Adopted for Diatomic Molecules

We adopt the following admittedly approximate model in the calculations of this paper. It is felt, however, that the model resembles reality sufficiently to give results of semiquantitative significance from which some definite conclusions can be drawn. We ignore the perturbation resulting from the surface on the internal vibrational degree of freedom, since this should be a second-order effect in most cases. That is, we assume that the partition function for this degree of freedom is the same as in the gas phase, and that
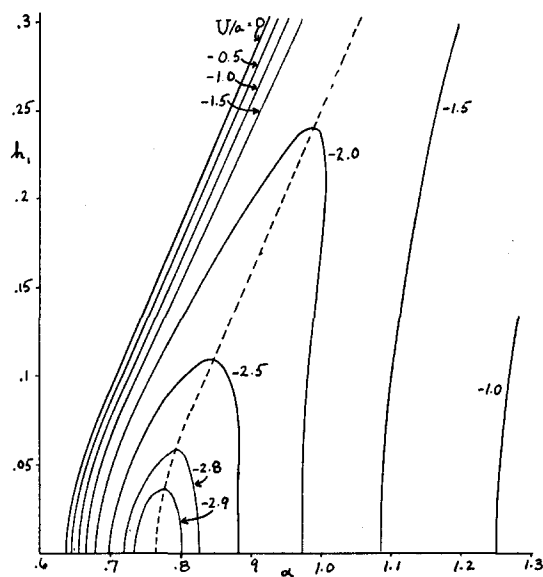


FIG. 1. Potential energy surface for $U/a$.

the two partition functions will cancel on taking ratios. The same assumption is made about the electronic partition function. We assume that the rotational and internal vibrational motions are separable, and we find the rotational properties from those of a rigid rotator with the equilibrium distance between atoms. In the absence of an alternative, we must assume that the van der Waals interaction of a diatomic molecule with an adsorbent molecule (or atom) can be obtained simply by adding the separate interaction caused by the two atoms of the diatomic molecule. In calculating the van der Waals interaction with the entire adsorbent, we integrate in the manner of London[6] instead of using the more refined procedure of summation.[7] Integration is used here because the considerable extra labor involved in summation is probably not justified at present in view of other approximations. In performing the integration the surface is assumed uniform. That is, we ignore here the (usually relatively small) periodic variation in energy of adsorption over the surface. For the two degrees of freedom parallel to the surface we assume free migration (localized adsorption is discussed in Section V). A more general partition function[2] for motion intermediate between free migration and localization could easily be substituted here (if one makes the implicit approximation that motion parallel to the surface is separable from other degrees of freedom), but free migration is the most important case.

The above are approximations connected with the model. (Even with this model approximations must be made in the actual calculations. These will be mentioned as they arise.) The following are restrictions made in the generality of the calculations. We shall actually write down equations and make calculations only for symmetrical diatomic molecules. The corresponding equations for unsymmetrical diatomic molecules (and, in fact, for any linear molecule) will be obvious. We shall use for the van der Waals interaction energy only terms of the form $r^{-6}$ and $r^{-12}$. Other terms could be introduced with-

[5] The frequency, $\nu$, of internal vibration for most diatomic molecules is of the order of $4 \times 10^{13}$ sec.$^{-1}$. The frequency of vibration of a molecule perpendicular to a surface (caused by surface forces) is of the order of $1 \times 10^{12}$ sec.$^{-1}$. In localized adsorption, the frequencies of vibration parallel to the surface are of the order of $3 \times 10^{11}$ sec.$^{-1}$. The latter frequencies are discussed in Section V.

[6] F. London, Zeits. f. physik Chemie **B11**, 222 (1930).
[7] S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, 1943). In Chapter VII there is a detailed discussion of integration *versus* summation for monatomic molecules.

out difficulty for interactions not properly represented by these expressions.

For purposes of comparison some calculations on monatomic molecules based on the above model (where it applies) are also discussed below.

## II. THE POTENTIAL ENERGY FUNCTION

Let the surface be the $xy$ plane, with $z$ increasing in the direction away from the adsorbent. Consider an atom at a distance $z = \rho$ from the surface. Let the potential energy of interaction of this atom with a single molecule (or atom) of the adsorbent at a distance $r$ be

$$u = u_0\left(\frac{r_0}{r}\right)^{12} - 2u_0\left(\frac{r_0}{r}\right)^{6}. \qquad (1)$$

We take infinite separation as the zero of energy throughout this paper. Suppose there are $N_0$ adsorbent molecules (or atoms) per cc. Then on straightforward integration over all values of $x$ and $y$, and those values of $z$ such that $z \leqslant 0$, one finds for the total interaction of the atom with the adsorbent

$$u_s = \frac{u_0 r_0^{12} \pi N_0}{45 \rho^9} - \frac{u_0 r_0^{6} \pi N_0}{3 \rho^3}. \qquad (2)$$

The attractive term was given by London.[6] Now if we have a rigid symmetrical diatomic molecule of interatomic distance $2d$ whose center is a distance $z$ $(z > d)$ from the surface, the axis of the molecule making an angle $\theta$ $(0 \leqslant \theta \leqslant \pi)$ with the $z$ axis, then the interaction of the molecule with the adsorbent is

$$U = a\left\{-\frac{1}{(\alpha+h_1)^3} - \frac{1}{(\alpha-h_1)^3} \right.$$
$$\left. +\frac{1}{15}\left[\frac{1}{(\alpha+h_1)^9} + \frac{1}{(\alpha-h_1)^9}\right]\right\}, \qquad (3)$$

where $a = u_0 r_0^3 \pi N_0/3$, $\alpha = z/r_0$, $h_1 = h_0 \cos\theta$, and $h_0 = d/r_0$. Equation (3) follows from Eq. (2) on adding the separate energies of interaction of the two atoms in the diatomic molecule. It should be emphasized that $u_0$ and $r_0$ characterize the interaction of only *one* atom of the diatomic molecule with a molecule of the adsorbent.

The function $U/a$ has been calculated and is shown in a contour diagram (potential energy
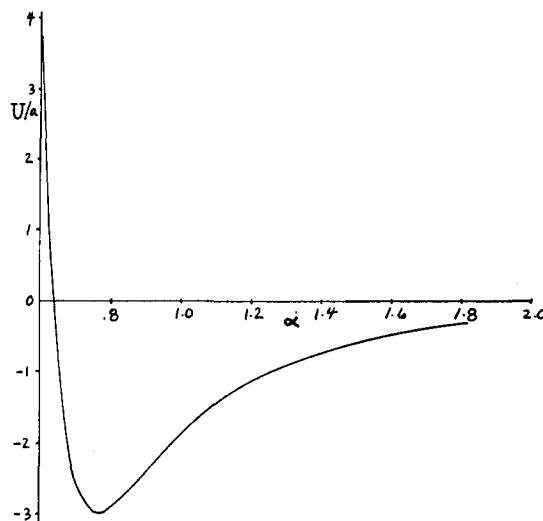
surface) in Fig. 1. The maximum value of $h_1$ in any particular case is, of course, $h_0$ (at $\theta = 0$). The figure is symmetrical about the line $h_1 = 0$ because of the symmetry of the molecule, so we have omitted negative values of $h_1$. The minimum value of $U/a$ is $-2.982$ and occurs at $\alpha = \alpha_0 = (1/5)^{1/6} = 0.7647$ and $h_1 = 0$. The potential energy curve along the line $h_1 = 0$ $(\theta = \pi/2)$ is shown in Fig. 2. The energy of adsorption (neglecting zero-point energy which is of the order of 100 cal./mole) is, according to this model, $\epsilon_1 = 2.982a$. For a typical numerical case (Section V) this turns out to be 2880 cal./mole, which is of the correct order of magnitude.

Using classical language, the physical situation associated with the potential energy surface, Fig. 1, is the following: the lowest energy occurs when the axis of the molecule is parallel $(\theta = \pi/2)$ to the surface (the potential energy $U$ is independent of the azimuthal angle $\varphi$ in this model) and the molecule is at a distance $z = z_0 = r_0\alpha_0 = 0.7647r_0$ from the surface. In order for the molecule to turn over, $h_1$ must increase from $h_1 = 0$ to $h_1 = h_0$ (i.e., $\theta$ must decrease from $\theta = \pi/2$ to $\theta = 0$). If the molecule turns over staying at the distance $\alpha = \alpha_0$ from the surface, the potential barrier involved is very large (56 kcal./mole in the numerical example of Section V). However, if the molecule moves away from the surface as it turns over, following the valley indicated by the dotted line in Fig. 1, the barrier

is the minimum barrier $U_0$ hindering rotation and is much smaller (1060 cal./mole in the example of Section V). This minimum barrier $U_0$ is plotted in Fig. 3 as a function of $h_0$.

## III. THE PARTITION FUNCTION FOR AN ADSORBED MOLECULE

We desire the partition function for a rigid rotator near a surface, with a potential energy function given by $U(z, \theta)$ in Eq. (3). The Hamiltonian is

$$H = \frac{p_x{}^2}{2M} + \frac{p_y{}^2}{2M} + \frac{p_z{}^2}{2M} + \frac{p_\theta{}^2}{2I} + \frac{p_\varphi{}^2}{2I \sin^2\theta} + U(z, \theta), \quad (4)$$

where $M$ is the mass of the molecule and $I$ the moment of inertia ($I = Md^2$ here). The correct procedure is to find the energy levels for such a molecule confined to an area $\alpha$ of the surface by solving Schrödinger's equation for the above Hamiltonian, and then form the partition function from these energy levels. This procedure appears to be impossible even for the present approximate model (the quantum-mechanical problem is discussed briefly in Appendix I). We must therefore turn to an approximate method. The approximation used here is the one suggested by Pitzer and Gwinn[8] for another type of problem. It is difficult to say what error is involved in using their approximation here. The error is no doubt greater than in the more re-



.5
$U_0/\epsilon_1$
.4

.3

.2

.1

     .1    .2  $h_o$  .3      .4       .5

FIG. 3. Potential barrier hindering rotation as a fraction of the heat of adsorption.

[8] K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942). It might be possible to use in problems of the sort being considered in this paper a new approximate method suggested by J. O. Halford, J. Chem. Phys. **15**, 645 (1947), based on the Wilson-Sommerfeld quantization rule.

stricted problem for which the approximation was originally designed, but certainly much smaller than the errors introduced by the model itself (compare the quantum-mechanical—using this approximation—and classical calculations of the partition function in the numerical example of Section V). The approximation is to write the partition function $f$ as

$$f = f_{\text{classical}} \times \frac{f_{\text{harmonic osc—quantal}}}{f_{\text{harmonic osc—classical}}}, \quad (5)$$

where $f_{\text{class}}$ is the classical partition function

$$f_{\text{class}} = \frac{1}{h^5} \int \cdots \int \exp(-H/kT) dx\,dy\,dz\,d\theta\,d\varphi$$
$$\times dp_x dp_y dp_z dp_\theta dp_\varphi, \quad (6)$$

and the other factors are partition functions calculated from the shape of the potential energy surface in the neighborhood of the minimum at $h_1 = 0$ and $\alpha = \alpha_0$.

Let us write down the harmonic oscillator expressions first. It may be helpful to refer to Appendix I in this connection. We expand $U/a$ in a Taylor's series about $\alpha = \alpha_0$, $h_1 = 0$, and find

$$U/a = -2.982 + 68.82[(\alpha - \alpha_0)^2 + h_1{}^2] + \cdots \quad (7)$$

with no cross product term of the form $h_1(\alpha - \alpha_0)$ (this is obvious from Fig. 1). Using Eq. (7) for $U/a$ in Eq. (6), one obtains

$$f_{\text{har osc-class}} = \frac{2\pi MkT}{h^2} \alpha \frac{2\pi(2\pi IkT)^{\frac{1}{2}}}{h} \frac{kT}{h\nu_z} \frac{kT}{h\nu_\theta}$$
$$\times \exp(2.982\beta), \quad (8)$$

where

$$\beta = a/kT,$$

$$\frac{h\nu_z}{kT} = \frac{8.296\beta^{\frac{1}{2}}h}{(2\pi MkT)^{\frac{1}{2}} r_0 \pi^{\frac{1}{2}}}, \quad (9)$$

$$\frac{h\nu_\theta}{kT} = \frac{8.296\beta^{\frac{1}{2}}hd}{(2\pi IkT)^{\frac{1}{2}} r_0 \pi^{\frac{1}{2}}}. \quad (10)$$

Actually, since $I = Md^2$ here, $\nu_z = \nu_\theta$. From Eq. (8) one can write immediately

$$f_{\text{har osc—quant}} = \frac{2\pi MkT}{h^2} \alpha \frac{2\pi(2\pi IkT)^{\frac{1}{2}}}{h}$$
$$\times [1 - \exp(-h\nu_z/kT)]^{-1}$$
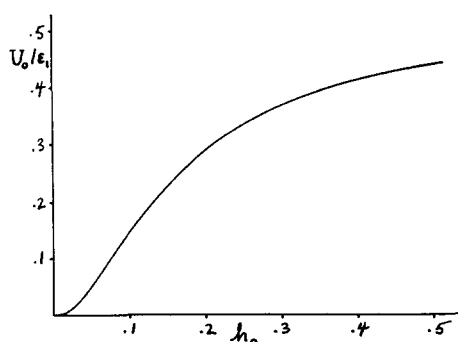$$\times [1 - \exp(-h\nu_\theta/kT)]^{-1}$$
$$\times \exp(2.982\beta). \quad (11)$$

TABLE I. Values of the function $q(\beta, h_1)$.

| $h_1$ ↓ \ $\beta$ → | 0.1 | 1 | 2 | 4 | 8 |
|---|---|---|---|---|---|
| 0.000 | 1.259 | 8.51 | 74.8 | 17420. | $17.78 \times 10^8$ |
| 0.025 | | | | 14860. | $12.82 \times 10^8$ |
| 0.050 | 1.240 | 7.86 | 58.8 | 9910. | $5.53 \times 10^8$ |
| 0.100 | 1.202 | 6.81 | 38.0 | 3530. | $0.67 \times 10^8$ |
| 0.200 | 1.144 | 5.55 | 20.4 | 712. | $0.02 \times 10^8$ |
| 0.300 | 1.103 | 5.00 | 15.31 | 309. | |
| 0.400 | 1.076 | 4.68 | 12.81 | 188. | |
| 0.500 | 1.057 | 4.51 | 11.61 | 142. | |

TABLE II. Values of the function $Q(\beta, h_0)$.

| $h_0$ ↓ \ $\beta$ → | 0.1 | 1 | 2 | 4 | 8 |
|---|---|---|---|---|---|
| 0.1 | 0.1236 | 0.779 | 5.80 | 1036. | $0.736 \times 10^8$ |
| 0.2 | 0.241 | 1.386 | 8.52 | 1193. | $0.757 \times 10^8$ |
| 0.3 | 0.353 | 1.911 | 10.26 | 1240. | $0.758 \times 10^8$ |
| 0.4 | 0.462 | 2.39 | 11.65 | 1264. | $0.758 \times 10^8$ |
| 0.5 | 0.568 | 2.85 | 12.86 | 1280. | $0.758 \times 10^8$ |

We now find $f_{\text{class}}$. Integration over $x$ and $y$ gives a factor $\alpha$, over $\varphi$ a factor $2\pi$, over $p_x$ and $p_y$ a factor $2\pi MkT$, over $p_\theta$ a factor $(2\pi IkT)^{\frac{1}{2}}$, and over $p_\varphi$ a factor $(2\pi IkT)^{\frac{1}{2}} \sin\theta$. So we have

$$f_{\text{class}} = \frac{2\pi MkT \, \alpha 4\pi^2 IkT}{h^5} \int\int\int [\exp(-U/kT)$$

$$\times \exp(-p_z{}^2/2MkT) \sin\theta \, d\theta \, dz \, dp_z]. \quad (12)$$

The question now arises as to what limits should be used for $\theta$, $z$, and $p_z$. We are interested here in an "adsorbed" molecule. By an "adsorbed" molecule we mean one whose $z$ motion is bound. That is, for any $\theta$, the $z$ motion is such that

$$U(z, \theta) + \frac{p_z{}^2}{2M} \leqslant 0, \quad (13)$$

or

$$p_z{}^2 \leqslant -2MU(z, \theta). \quad (14)$$

The limits on $p_z$ are, therefore, $\pm[-2MU(z, \theta)]^{\frac{1}{2}}$. The momenta $p_x$, $p_y$, $p_\theta$, and $p_\varphi$ have no such restriction. Further, since $p_z{}^2/2M \geqslant 0$ in any case, we integrate only over those values of $\theta$ and $z$ such that $U(z, \theta) \leqslant 0$. There is, finally, the restriction that $0 \leqslant \theta \leqslant \pi$. Referring to Fig. 1, we integrate between the $U=0$ contour and $z = \infty$ along the strip between $h_1 = -h_0$ and $h_1 = h_0$. The integral over $p_z$ is

$$\int_{-(-2MU)^{\frac{1}{2}}}^{(-2MU)^{\frac{1}{2}}} \exp(-p_z{}^2/2MkT) dp_z$$

$$= (2\pi MkT)^{\frac{1}{2}} \operatorname{erf}(-U/kT)^{\frac{1}{2}} \quad (15)$$

where $\operatorname{erf} x$ is the error function

$$\operatorname{erf} x = \frac{2}{(\pi)^{\frac{1}{2}}} \int_0^x e^{-t^2} dt. \quad (16)$$

Equation (12) becomes

$$f_{\text{class}} = \left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} \alpha \frac{8\pi^2 IkT}{h^2} \frac{r_0}{h_0} \int\int_{\substack{0 \leqslant h_1 \leqslant h_0 \\ U \leqslant 0}}$$

$$\times \exp(-U/kT) \operatorname{erf}(-U/kT)^{\frac{1}{2}} d\alpha \, dh_1. \quad (17)$$

In this equation we shall refer to the integral over $\alpha$ for fixed $h_1$ as $q(\beta, h_1)$. Values of $q(\beta, h_1)$ were obtained by using numerical integration out to a sufficiently large value of $\alpha$ and then analytical integration to $\alpha = \infty$. The values of the double integral, which we shall call $Q(\beta, h_0)$, were found by interpolating and integrating (numerically) $q$ from $h_1 = 0$ to $h_1 = h_0$. The calculated values of $q$ and $Q$ are given in Tables I and II, respectively.

The asymptotic expressions for $q(\beta, 0)$ and $Q(\beta, h_0)$, for large $\beta$, are useful:

$$\lim_{\beta \to \infty} q(\beta, 0) = \frac{\exp(2.982\beta)}{4.679\beta^{\frac{1}{2}}}, \quad (18)$$

$$\lim_{\beta \to \infty} Q(\beta, h_0) = \frac{\exp(2.982\beta)}{43.81\beta}. \quad (19)$$

These are found from Eqs. (7) and (8).

If these results are now substituted into Eq. (5), we have (we now include, for completeness: $\rho$, the nuclear spin weight; $\sigma = 2$, the symmetry number; $j_{\text{el}}$, the electronic partition function; and $j_{\text{vib}}$, the partition function for internal vibration)

$$f = \frac{\rho^2}{2} j_{\text{el}} j_{\text{vib}} \frac{2\pi MkT}{h^2} \alpha \left[\frac{43.81\beta Q(\beta, h_0)}{\exp(2.982\beta)}\right]$$

$$\times \frac{2\pi(2\pi IkT)^{\frac{1}{2}}}{h} [1 - \exp(-h\nu_z(kT)]^{-1}$$

$$\times [1 - \exp(-h\nu_\theta/kT)]^{-1} \exp(2.982\beta). \quad (20)$$

## IV. THE BET CONSTANT $C$

The fundamental parameter in the BET adsorption isotherm[9] is

$$C = \frac{a_1 b_2}{b_1 a_2} \exp[(\epsilon_1 - \epsilon_L)/kT], \quad (21)$$

where $-\epsilon_1$ is the energy of an isolated molecule in the first adsorbed layer, $-\epsilon_L$ is the energy of a molecule in the liquid state, and $a_1 b_2/b_1 a_2$ is a kinetic factor. In actual applications of Eq. (21) to experimental data it appears to be the custom to put $\Lambda$, the heat of vaporization of the liquid, in place of $\epsilon_L$, without altering $a_1 b_2/b_1 a_2$. From the statistical derivations[10,1-3] of the BET equation it is clear that these two quantities should not be confused. The (theoretical) connection between them depends on which theory of liquids is referred to. $\Lambda = \epsilon_L - kT/2$ is probably approximately correct,[11] so $a_1 b_2/b_1 a_2 \cong Re^{\frac{1}{2}}$ (see Eq. (22)). It is actually $R$ and not $a_1 b_2/b_1 a_2$ which has been set equal to unity in applications, but the difference is perhaps not very important.

We can avoid the above uncertainty resulting from the lack of an adequate theory of liquids and also have $C$ in the form actually used in analysis of experimental data by writing

$$C = R \exp[(\epsilon_1 - \Lambda)/kT]. \quad (22)$$

The purpose of this section is to obtain expressions for $R$.

We consider for convenience adsorption at very low pressures, so that the adsorbed molecules form a two-dimensional perfect gas with no interactions between themselves. If $N$ molecules are adsorbed on an area, $\alpha$, the partition function for the system is $f^N/N!$, where $f$ is given by Eq. (20). The chemical potential of the adsorbed molecules is then

$$\frac{\mu_A}{kT} = -\frac{\partial \ln(f^N/N!)}{\partial N} = -\ln f + \ln N. \quad (23)$$

For molecules in the vapor phase at a pressure $p$

$$\frac{\mu_G}{kT} = \ln p + \ln\left[\left(\frac{h^2}{2\pi MkT}\right)^{\frac{3}{2}} \frac{1}{kT j_i}\right], \quad (24)$$

[9] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[10] A. B. D. Cassie, Trans. Faraday Soc. **41**, 450 (1945).
[11] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, England, 1939), Chapter VIII.

where

$$j_i = \frac{\rho^2}{2} j_{\text{el}} j_{\text{vib}} \frac{8\pi^2 IkT}{h^2}. \quad (25)$$

At equilibrium,

$$\frac{\mu_A}{kT} = \frac{\mu_G}{kT},$$

so that

$$N = pf\left(\frac{h^2}{2\pi MkT}\right)^{\frac{3}{2}} \frac{1}{kT j_i}. \quad (26)$$

Let $N^0$ be the maximum number of molecules that can be adsorbed in the first layer, let $p_0$ be the vapor pressure at the temperature $T$ of the gas being adsorbed, let $x = p/p_0$ and $\theta = N/N^0$. Then our low pressure isotherm can be written

$$\theta = Cx, \quad (27)$$

with

$$C = \frac{f}{N^0 j_i} \frac{p_0}{kT}\left(\frac{h^2}{2\pi MkT}\right)^{\frac{3}{2}}. \quad (28)$$

This expression for $C$ is rather general (for adsorption at higher pressures $C$ is the same but the isotherm is more complicated[2]). It holds[2] for both localized and mobile adsorption and for any type of molecule. The appropriate $f$ must, of course, be substituted. Equation (26) is even more general, since it has meaning for temperatures above the critical temperature of the gas being adsorbed.

For the particular case we are interested in here, we substitute Eqs. (20) and (25) into Eq. (28), and put $p_0 = \delta \exp(-\Lambda/kT)$ and $2.982\beta = \epsilon_1/kT$. This gives $C$ in the form of Eq. (22) with

$$R = \pi^{\frac{1}{2}}\left(\frac{h^2}{2\pi MkT}\right)^{\frac{1}{2}}\left(\frac{h^2}{8\pi^2 IkT}\right)^{\frac{1}{2}} \frac{\alpha}{N^0} \frac{\delta}{kT}$$

$$\times\left[\frac{43.81\beta Q(\beta, h_0)}{\exp(2.982\beta)}\right][1 - \exp(-h\nu_z/kT)]^{-1}$$

$$\times[1 - \exp(-h\nu_\theta/kT)]^{-1}. \quad (29)$$

The substitution for $p_0$ is justified both experimentally and theoretically.[11] For non-polar molecules $\delta \cong 2.7_4 \times 10^{10}$ ergs/cc.

We now consider certain special cases of Eq. (29). In a completely classical calculation we would use Eq. (17) instead of Eq. (5). This gives

$$R = \frac{\alpha}{N^0} \frac{\delta}{kT} \frac{Q(\beta, h_0)}{\exp(2.982\beta)} \frac{r_0}{h_0}. \quad (30)$$

If we assume that the rotation of the molecules is unaffected by the surface (i.e., that $U$ is effectively independent of $\theta$), the rotational partition functions for the gaseous and adsorbed phases will cancel. If we then use for the potential energy for all values of $\theta$ the function $U(z, \pi/2)$, and employ (for purposes of comparison) the approximation of Pitzer and Gwinn[3] for the $z$ motion, the same argument as above for the more general problem leads here to (omitting $j_{\text{rot}}$)

$$f_{\text{har osc-class}} = \frac{2\pi MkT}{h^2}\,\alpha\,\frac{kT}{h\nu_z}\,\exp(2.982\beta),\qquad(31)$$

$$f_{\text{har osc-quant}} = \frac{2\pi MkT}{h^2}\,\alpha[1-\exp(-h\nu_z/kT)]^{-1}$$
$$\times\exp(2.982\beta),\qquad(32)$$

$$f_{\text{class}} = \left(\frac{2\pi MkT}{h^2}\right)^{\frac{1}{2}}\alpha r_0 q(\beta, 0),\qquad(33)$$

and

$$R = \left(\frac{h^2}{2\pi MkT}\right)^{\frac{1}{2}}\frac{\alpha}{N^0}\frac{\delta}{kT}\left[\frac{4.679\beta^{\frac{1}{2}}q(\beta, 0)}{\exp(2.982\beta)}\right]$$
$$\times[1-\exp(-h\nu_z/kT)]^{-1}.\qquad(34)$$

Equation (34) is also the expression for $R$ for a monatomic molecule based on the methods of the present paper, but with one important alteration: when Eq. (34) is used for a monatomic molecule, $\beta = a/kT$ as before, but $a = u_0 r_0^3 \pi N_0/6$, where $u_0$ and $r_0$ refer to the interaction of the monatomic molecule with a molecule (or atom) of the adsorbent. This expression for $a$ differs by a factor of two from the earlier one (Eq. (3)). In fact, Eq. (34) may be used for any mobile adsorbed molecule, however large, if one can neglect the effect of the surface on internal degrees of freedom (rotation, vibration, electronic) and uses

$$a = u_0 r_0^3 \pi N_0/6,$$

$u_0$ and $r_0$ referring to the interaction of an adsorbed *molecule* with a molecule (or atom) of the adsorbent.

For localized adsorption we must replace[2] the $xy$ partition function

$$\frac{2\pi MkT}{h^2}\alpha \quad \text{by} \quad N^0[1-\exp(-h\nu/kT)]^{-2},$$

where $\nu = \nu_x = \nu_y$ is the frequency of vibration parallel to the surface:

$$\nu = (V_0/4Ms^2)^{\frac{1}{2}}.\qquad(35)$$

In Eq. (35), $V_0$ is the maximum[2] potential barrier (of the order of, say, 0.3–1.0 kcal./mole), and $s$ is the distance between potential minima along both $x$ and $y$ axes (the surface lattice being assumed simple cubic). Let $R_l$ be the value of $R$ for localized adsorption. Then, for any of the cases above, we can get $R_l$ from $R$ by using

$$R_l = \frac{h^2}{2\pi MkT}\frac{1}{s^2}[1-\exp(-h\nu/kT)]^{-2}R.\quad(36)$$

We have substituted $s^2 = \alpha/N^0$ in writing Eq. (36).

The approximate temperature dependence of $R$ is of some interest. It is easily seen from the above equations that for mobile adsorption $R$ is roughly temperature independent for a symmetrical diatomic molecule (Eq. (29)), and $R$ varies approximately at $T^{-\frac{1}{2}}$ for a monatomic molecule or for any molecule whose internal degrees of freedom are essentially unperturbed by the surface (Eq. (34)). For localized adsorption, the temperature dependence in the two cases above is approximately as $T$ and $T^{\frac{1}{2}}$, respectively, (Eq. (36)).

## V. A NUMERICAL EXAMPLE

It is desirable to get an idea of the orders of magnitude involved in the above equations. To do this, we give numerical results for a (hypothetical) case which is very average. Let us take $N_0 = 1\times10^{23}$ cc.$^{-1}$, $u_0 = 15\times10^{-15}$ erg, $r_0 = 3.5$A, $T = 244°$K, $M = 50$ molecular weight units, $d = 1.05$A, $\alpha/N^0 = 20$A$^2$ and $\delta = 2.74\times10^{10}$ ergs/cc. Some derived quantities of interest for this example are then $\epsilon_1 = 2880$ cal./mole, $\beta = 2$, $h_0 = 0.30$, $U_0 = 1060$ cal./mole (as compared to $kT = 485$ cal./mole, so that rotation is restricted considerably), $Q = 10.26$, $43.81\beta Q/\exp(2.982\beta) = 2.31$, and $\nu_z = \nu_\theta = 1.52\times10^{12}$ sec.$^{-1}$. The "correct" value of $R$ obtained from Eq. (29) is 6.71. A completely classical calculation of $R$ (Eq. (30)) gives $R = 5.01$. This differs so little from the quantum-mechanical value that one can probably conclude that the use of the approximation of Pitzer and Gwinn is not very serious. If we

assume that the rotational partition function is unaffected by the surface, and use Eq. (34), we find $R = 12.7$. The suppression of rotation in this example therefore decreases $R$ by a factor of about two. If the adsorption is localized, taking $V_0 = 1000$ cal./mole (which is a rather large value), we find from Eq. (35) $\nu = \nu_x = \nu_y = 3.24 \times 10^{11}$ sec.$^{-1}$ and $R_l = 0.326R = 0.326 \times 6.71 = 2.19$ from Eq. (36).

Cassie[10] has published some rather frequently quoted calculations in which he finds $R$, or rather $R_l$ since he assumes localized adsorption, to be of the order of $1/50$ or less. This is just the right order of magnitude to account for the extent to which the derived values of the heat of adsorption are found to be too low (on applying the BET equation assuming $R = 1$). However, on the basis of the calculations outlined above,[12] the present writer is forced reluctantly to form the opinion that Cassie's explanation is not correct and that some other one will have to be found. The reasons Cassie found $R = 1/50$ (or less) instead of $R = 5 - 10$ are the following: (1) he assumed localized adsorption (which would actually cut the value of $R = 5 - 10$ down only to about[13] $R_l = 2$, even taking a rather large value for $V_0$), and (2) the remaining factor of 100 (or more) between $1/50$ (or less) and two arises because Cassie used $\nu_x = \nu_y = \nu_z = 4 \times 10^{12}$ sec.$^{-1}$, which would appear to be too high by a factor of about 10 for both $\nu_x$ and $\nu_y$ and perhaps another factor of two to four for $\nu_z$. Several other frequencies may be mentioned for comparison: the value of $\nu_x = \nu_y$ for the adsorption of argon on potassium chloride is[2] $3.3 \times 10^{11}$ sec.$^{-1}$, using $V_0 = 400$ cal./mole. Orr[14] found $\nu_z = 1 \times 10^{12}$ sec.$^{-1}$ in his very refined calculations on the adsorption of argon by potassium chloride. In any case, as emphasized in the second paper of this series,[2] it is, in general, incorrect to consider physical adsorption as localized.

There will, of course, be a range in possible values of $R$ calculated from the above equations.

Most cases of interest will probably fall within a factor of five (larger or smaller) of the values given above for an average example. One can estimate this range by noting that the *approximate* dependence of $R$ (mobile adsorption) on the fundamental parameters is given by (Eq. (29))

$$R \cong \text{const.} \times \left(\frac{\alpha}{N^0}\right) \frac{1}{d u_0 r_0 N_0}$$

for a symmetrical diatomic molecule, or by (Eq. (34))

$$R \cong \text{const.} \times \left(\frac{\alpha}{N^0}\right) \frac{1}{T^{\frac{1}{2}} u_0^{\frac{1}{2}} r_0^{\frac{1}{2}} N_0^{\frac{1}{2}}}$$

for a monatomic molecule (or any molecule with rotation not much affected by the surface). We may note that the mass does not occur in either of these equations (the temperature has already been discussed).

One final remark on generality: it is fairly obvious that the general conclusions reached in this paper for symmetrical diatomic molecules will also hold for slightly unsymmetrical diatomic molecules. Also, the most favorable case for neglecting the effect of the surface on rotation of a complicated molecule is for a symmetrical molecule such as $CH_4$ or $CCl_4$. The behavior of a very unsymmetrical diatomic molecule (for example HCl) can be quite different in some respects. This case will be investigated.

### APPENDIX I

On writing down the Schrödinger equation associated with Eq. (4), one can put $\psi = F(x, y)\Phi(\varphi)\chi(z, \theta)$, and then obtain the energy levels for a particle of mass $M$ in a two-dimensional box from the $F$ equation and, as usual, find

$$\Phi_m(\varphi) = \frac{1}{(2\pi)^{\frac{1}{2}}} \exp(im\varphi), \quad m = 0, \pm 1, \pm 2, \cdots \quad (37)$$

from the $\Phi$ equation. The $\chi$ equation is

$$\frac{I}{M} \frac{\partial^2 \chi}{\partial z^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \chi}{\partial \theta}\right) - \frac{m^2}{\sin^2\theta}\chi$$
$$+ \frac{8\pi^2 I}{h^2}[E - U(z, \theta)]\chi = 0, \quad (38)$$

where $E_{\text{total}} = E + E_{xy}$. There appears to be little hope of finding the energy eigenvalues of Eq. (38) for the $U(z, \theta)$ given by Eq. (3). However, in the limiting case of harmonic oscillations about the potential minimum, the solution is, of course, easy. We substitute in this case Eq. (7) into

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[12] Even considering the roughness of the model the values of $R$ given here ought to be accurate at least to within a factor of two. The heat of adsorption $\epsilon_1$ from this model is probably accurate[7] to about a factor of two, and $R$ should be much less sensitive than $\epsilon_1$.

[13] It is interesting that $R_l$ and hence $a_1 b_2 / b_1 a_2$ is not far from unity here. This is just the assumption made in the original BET theory (*localized* adsorption).

[14] W. J. C. Orr, Trans. Faraday Soc. **35**, 1247 (1939).

Eq. (38), put $\chi = \Theta(\theta)Z(z)$, and find

$$Z'' + \frac{8\pi^2 M}{h^2}\left(E_z - \frac{68.82az^2}{r_0^2}\right)Z = 0, \qquad (39)$$

and

$$\Theta'' + \frac{\cos\theta}{\sin\theta}\Theta' - \frac{m^2\Theta}{\sin^2\theta} \\ + \frac{8\pi^2 I}{h^2}\left(E_{\theta\varphi} - \frac{68.82ad^2\cos^2\theta}{r_0^2}\right)\Theta = 0, \quad (40)$$

where $E + 2.982a = E_z + E_{\theta\varphi}$. The energy levels $E_z$ are

$$E_z = (n_z + \tfrac{1}{2})h\nu_z, \quad n_z = 0, 1, 2, \cdots, \qquad (41)$$

where $\nu_z$ is given by Eq. (9). For the limiting case of interest here put, in Eq. (40), $\theta - (\pi/2) = \xi$, $\Theta(\theta) = G(\xi)$, $\sin\theta = 1$, and $\cos\theta = -\xi$. Then, dropping the term in $\Theta'$ ($\xi$ small, $a$ large), we have

$$G'' + \frac{8\pi^2 I}{h^2}\left(E_{\theta\varphi} - \frac{h^2 m^2}{8\pi^2 I} - \frac{68.82ad^2\xi^2}{r_0^2}\right)G = 0. \qquad (42)$$

The energy levels are $E_{\theta\varphi} = E_\theta + E_\varphi$ with

$$E_\theta = (n_\theta + \tfrac{1}{2})h\nu_\theta, \quad n_\theta = 0, 1, 2, \cdots, \qquad (43)$$

$$E_\varphi = \frac{m^2 h^2}{8\pi^2 I}, \qquad m = 0, \pm1, \pm2, \cdots, \qquad (44)$$

in which $\nu_\theta$ is given by Eq. (10). The lowest eigenvalue for the general Eq. (38) is given approximately by the lowest eigenvalue in the harmonic oscillator limiting case: $E \cong -2.982a + h\nu_z/2 + h\nu_\theta/2 \cong E_{\text{total}}$. This is the negative of the heat of adsorption (including properly the zero-point energy).

## APPENDIX II

In calculating surface areas using the BET method, it is necessary to adopt a value for the area occupied per molecule when the surface is completely filled with one layer. This value is usually obtained from the density of

TABLE III. Surface area per molecule in $A^2$.

| | Liquid density value | $b'$ |
|---|---|---|
| $N_2$ | 16.2 | 15.4 |
| $O_2$ | 14.1 | 13.5 |
| A | 14.4 | 13.6 |
| CO | 16.8 | 15.6 |
| $CO_2$ | 17.0 | 16.5 |
| $CH_4$ | 18.1 | 16.4 |
| $n\text{-}C_4H_{10}$ | 32.1 | 33.0 |
| $NH_3$ | 12.9 | 15.0 |
| NO | 12.5 | 12.5 |
| $N_2O$ | 16.8 | 16.9 |
| $n\text{-}C_7H_{16}$ | 45.0 | 47.0 |
| $H_2O$ | 10.5 | 13.1 |

the liquid. There is an alternative procedure that may be of interest. The values obtained do not differ much from the liquid density values.

If we use van der Waals' equation as the equation of state of the monolayer and also of the gas phase, it has been shown[2] that the surface area per molecule when the first layer is full is $b'$, the two-dimensional van der Waals constant, and that $b'$ is related to the three-dimensional van der Waals constant $b$ by

$$b' = \frac{\pi}{2}\left(\frac{3b}{2\pi}\right)^{\tfrac{2}{3}}. \qquad (45)$$

Now $b = kT_c/8P_c$, where $T_c$ and $P_c$ are the three-dimensional critical temperature and pressure, so one can write finally

$$b' = 6.354\left(\frac{T_c}{P_c}\right)^{\tfrac{2}{3}} \text{ (in units of } A^2), \qquad (46)$$

where $P_c$ is in atmospheres. In Table III the values of $b'$ for a number of gases, calculated from the critical temperatures and pressures, are compared with the commonly used liquid density values.