

Statistical Mechanics of Adsorption. VIII. The Statistical Analogue of the B.E.T. Constant a $1/b$ $1/a$ 2 for Simulated Benzene and Hydrogen Iodide Molecules on Graphite

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Statistical Mechanics of Adsorption. VIII. The Statistical Analogue of the B.E.T. Constant a_1b_2/b_1a_2 for Simulated Benzene and Hydrogen Iodide Molecules on Graphite

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The approximate study of the restricted rotation of molecules near a surface is extended to an unsymmetrical diatomic molecule, hydrogen iodide, and a ring molecule, benzene, for a graphite surface in each case. Calculations of the factor R in the BET constant $C = R \exp(\epsilon_1 - \Lambda)/kT$ are carried out for these cases. R is found to be of the same order of magnitude (2-20) as for the symmetrical diatomic molecule.

I. INTRODUCTION

IN a theoretical treatment of the statistical mechanics of adsorption, it is of interest to consider the effect which the surface has upon the adsorbed molecule. At low pressures, the general adsorption equation $v/v_m = Cx$ is valid, where v is the volume of gas adsorbed, v_m is the volume of gas which can be adsorbed in a complete monomolecular layer, and $x = p/p_0$, the ratio of the gas pressure to the vapor pressure for the temperature existing in the system. C , the fundamental parameter, is given by

$$C = R \exp(\epsilon_1 - \Lambda)/kT$$

with Λ the heat of vaporization of the liquid and $-\epsilon_1$ the energy of an isolated molecule in its ground state relative to infinite separation from the surface as the zero of energy. Since R depends upon the partition functions of the molecule as a gas and as an adsorbate, the effect of the adsorbing surface upon the molecule adsorbed is worthy of study.

This problem has been treated by Hill¹ for the case of a symmetrical diatomic molecule. The purpose of this paper is to make a similar study for two other cases: *A* an unsymmetrical diatomic molecule, and *B* a molecule representable by a ring. In order to make the results more tangible, calculations have been carried out for two molecules which have been studied experimentally to some extent: hydrogen iodide^{2,3} and benzene.⁴⁻⁷ A smooth, non-polar surface which does not react chemically with the gas to be adsorbed is postulated; for this graphite has been chosen as the model.

The general method and the assumptions are the same as those in Hill's paper. Thus, a van der

Waals interaction equation of the form

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

is assumed to represent the interaction between each atom of the molecule to be adsorbed and a single molecule of the adsorbent. Here u is the energy of interaction, r is the distance between the atom of gas and the surface molecule, r_0 is the equilibrium distance between the two, and u_0 is the interaction energy corresponding to the distance r_0 . The van der Waals interaction of the gas molecule with a single adsorbent molecule is assumed to be the sum of the atomic interactions of this type. To calculate the interaction of the gas molecule with the entire adsorbent, integration in the manner of London⁸ is employed, instead of the more refined and more laborious procedure of summation. The partition function for internal vibrations of the molecule to be adsorbed is assumed to be identical in the gas and adsorbate phases; i.e., the perturbation on these particular degrees of freedom resulting from the surface is ignored. The surface is considered uniform in that no periodic variation of the energy of adsorption over the surface is postulated. Free migration over the surface (mobile adsorption) is also assumed. The use of Eq. (1) predicates that there are no electrostatic effects to be considered; terms to take these into account could be introduced, but, in view of the hypothetical nature of the problem resulting from the above assumptions, the extra labor involved seems unwarranted.

Hydrogen iodide has been chosen as an example of case *A* because it is very unsymmetrical, yet has only a small dipole moment⁹ (0.38×10^{-18} e.s.u.) and thus little ionic character. Benzene is certainly the most obvious example for case *B*.

II. CASE A: SIMULATED HYDROGEN IODIDE

Let the diatomic molecule have atoms, with masses m_1 and m_2 , separated by a constant dis-

¹ Terrell L. Hill, *J. Chem. Phys.* **16**, 181 (1948).

² M. Dubinin, *Zeits. f. physik. Chemie* **123**, 86 (1926).

³ L. H. Reyerson and C. Bemmels, *J. Phys. Chem.* **46**, 35 (1942).

⁴ A. S. Coolidge, *J. Am. Chem. Soc.* **46**, 596 (1924).

⁵ B. Lambert and A. M. Clark, *Proc. Roy. Soc. A* **122**, 497 (1929).

⁶ W. G. Palmer, *Proc. Roy. Soc. A* **168**, 190 (1938).

⁷ C. Kemball and E. K. Rideal, *Proc. Roy. Soc. A* **187**, 53 (1946); *ibid.* **A190**, 117 (1947).

⁸ F. London, *Zeits. f. physik. Chemie* **B11**, 222 (1930).

⁹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945).

tance d . Let the perpendicular distance from the center of gravity of the molecule to the surface be $z = \rho$. Let θ be the angle between z and the line connecting the centers of the atoms. Let the surface of the adsorbent be the xy plane, with z negative in the adsorbent. Let ϕ be the angle between the plane containing the nuclei and the z axis, and the xz plane; a change in ϕ then represents a rotation of the molecule about the z axis. It is obvious that a change of ϕ does not affect the distance of either atom from the surface, so that for a uniform

TABLE I. Atomic interactions.

		N(C)	H	I
T_c ($^{\circ}\text{K}$)		126.0	—	826.1
u_0 (molecule)	$\times 10^{15}$ ergs	13.61	4.25	89.22
u_0 (atom)	$\times 10^{15}$ ergs	6.60	2.06	43.26
u_0 (atom to carbon)	$\times 10^{15}$ ergs	6.60	3.687	16.90

surface a rotation of this type has no effect upon the van der Waals interaction energy. Let r_{01} and r_{02} be the equilibrium van der Waals distances of the two atoms from a surface molecule; i.e., r_{01} is the sum of the van der Waals radii of atom 1 and of a surface molecule. Let ρ_1 and ρ_2 be the perpendicular distances of these atoms from the surface. Let N_0 be the number of adsorbent molecules per cc.

In (1), r is a function of the coordinates x , y , and z of the adsorbent molecule; $r = (x^2 + y^2 + [z - \rho]^2)^{1/2}$. If we integrate (1) over all values of x and y , and over those values of z such that $z \leq 0$, we will have approximated the interaction of one atom of the diatomic molecule with the entire adsorbent. Such integration gives

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

The interaction of the entire molecule with the adsorbent will be the sum of two such terms:

$$U = \frac{u_{01} r_{01}^{12} \pi N_0}{45 \rho_1^9} - \frac{u_{01} r_{01}^6 \pi N_0}{3 \rho_1^3} + \frac{u_{02} r_{02}^{12} \pi N_0}{45 \rho_2^9} - \frac{u_{02} r_{02}^6 \pi N_0}{3 \rho_2^3}.$$

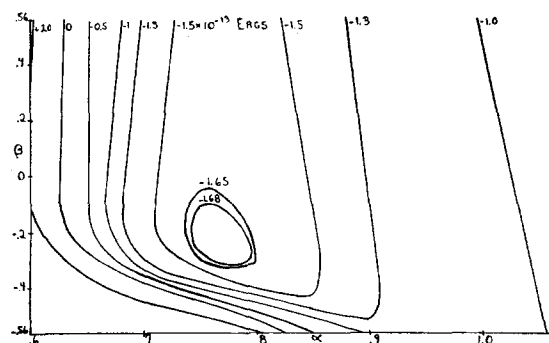


FIG. 1.

It is apparent that

$$\rho_1 = z + \frac{m_2 d \cos \theta}{m_1 + m_2} \quad \text{and} \quad \rho_2 = z + \frac{m_1 d \cos \theta}{m_1 + m_2}.$$

Making this substitution and letting

$$a_1 = u_{01} r_{01}^3 \pi N_0 / 3, \quad a_2 = u_{02} r_{02}^3 \pi N_0 / 3, \quad \alpha_1 = z / r_{01},$$

$$\alpha_2 = z / r_{02}, \quad \beta_1 = \frac{m_2 d \cos \theta}{r_{01}(m_1 + m_2)}, \quad \text{and} \quad \beta_2 = \frac{m_1 d \cos \theta}{r_{02}(m_1 + m_2)},$$

we find

$$U = a_1 \left(\frac{1}{15(\alpha_1 - \beta_1)^9} - \frac{1}{(\alpha_1 - \beta_1)^3} \right) + a_2 \left(\frac{1}{15(\alpha_2 + \beta_2)^9} - \frac{1}{(\alpha_2 + \beta_2)^3} \right). \quad (2)$$

For the particular case of hydrogen iodide, $m_2 / (m_1 + m_2) = 0.0079$. For α of the order of 1, we may then approximate $\alpha_1 - \beta_1$ by α_1 . This is equivalent to saying that the iodine atom is essentially the center of mass of the hydrogen iodide molecule.

Pauling⁹ and Stuart¹⁰ give the van der Waals radii of hydrogen as 1.2, carbon as 1.67, and iodine as 2.07 Å. Then $r_{0 \text{ CI}} = 1.67 + 2.07 = 3.74$ Å, and $r_{0 \text{ CH}} = 1.67 + 1.2 = 2.87$ Å. Then

$$\frac{\alpha_2}{\alpha_1} = \frac{z/2.87}{z/3.74} = 1.303.$$

Let us replace α_1 by α and α_2 by 1.303α . The interatomic distance, d , for hydrogen iodide⁹ is 1.62 Å. Then Eq. (2) becomes

$$U = a_1 \left(\frac{1}{15\alpha^9} - \frac{1}{\alpha^3} \right) + a_2 \left(\frac{1}{15(1.303\alpha + 0.560 \cos \theta)^9} - \frac{1}{(1.303\alpha + 0.560 \cos \theta)^3} \right).$$

Let us next find the position of minimum energy; this involves taking derivatives of $U(\alpha, \theta)$ with respect to α and to θ , and setting each to 0. The results are $\alpha = (\frac{1}{3})^{1/6} = 0.7647$, and $\theta = 114^\circ 34'$. The molecule is then in the most stable position when the iodine atom is at a distance from the surface equal to 0.7647 times the sum of the van der Waals radii of carbon and iodine; it may readily be shown that, with $\theta = 114^\circ 34'$, the hydrogen atom is also a distance 0.7647 times the sum of the van der Waals radii of carbon and hydrogen from the surface. This value of 0.7647 r_0 is the same result found for

¹⁰ H. A. Stuart, *Molekülstruktur* (Verlag Julius Springer, Berlin, 1934).

TABLE II. Integration for HI at 81.33°K.

β	$f(\beta)$	$\int f(\beta)d\beta$
0.56	1.390×10^5	
0.53	1.415	
0.50	1.433	8483
0.4	1.555	
0.3	1.720	
0.2	1.913	
0.1	2.180	
0.0	2.540	
-0.1	3.214	121595
-0.15	3.635	
-0.20	3.882	
-0.25	3.990	
-0.30	3.336	
-0.35	1.710	
-0.40	0.844	
-0.45	0.460	
-0.50	0.177	91159
-0.53	0.080	
-0.56	0.000	497
		$Q(T) = 2.217 \times 10^5$

the symmetrical diatomic molecule and for the monatomic case, as expected.

a_1 and a_2 should next be evaluated. $a_1 = u_0 \text{ CI} r^3_0 \text{ CI} N_0/3$, and for graphite $N_0 = 1.128 \times 10^{23}$ atoms per cc. To find u_0 , the following method may be adopted. Values of the critical temperatures of I_2 and of N_2 are selected. (N_2 is used as the best substitute for C_2 for which no data are available.) Then the assumption $u_0 = 0.1080 T_c \times 10^{-15}$ ergs, for symmetrical non-polar molecules, is made on the basis of Hill's calculations.¹¹ The contribution of each atom to u_0 is taken to be 16/33 of the total for a symmetrical diatomic molecule.¹¹ Then the interaction energy is assumed to be the geometric mean of the atomic values thus obtained: $u^2_0 \text{ CI} = u_{0\text{CI}} u_{0\text{I}}$. The values used are shown in Table I. The value given for u_0 for hydrogen is taken from Hill's paper. This procedure is admittedly a very rough approximation, but it is employed in the absence of a better available method. Use of these values leads to $a_1 = 1.044 \times 10^{-13}$ and $a_2 = 1.030 \times 10^{-14}$ erg per molecule.

Equation (3) may now be used to calculate a potential energy surface for the hydrogen iodide molecule near the graphite surface. The results are shown graphically in Fig. 1. U_0 , the potential energy at the position of minimum energy ($\alpha_0 = 0.7647$; $\theta_0 = 114^\circ 34'$), is -1.710×10^{-13} erg per molecule (2460 calories per mole). The potential energy surface is of course not symmetrical. However, crudely we may say that as the hydrogen atom revolves away from the surface, the system tries to remain in the potential energy valley by having the iodine atom move slightly nearer the surface at first. For a complete rotation (in θ) of the molecule about its center of gravity, an energy barrier of about 520 calories per mole must be over-

¹¹ Terrell L. Hill, J. Chem. Phys. 16, 399 (1948).

TABLE III. Integration for HI at 244°K.

β	$f(\beta)$	$\int f(\beta)d\beta$
0.56	23.95	
0.53	24.28	
0.5	24.63	1.46
0.4	25.92	
0.3	27.22	
0.2	28.64	
0.1	30.02	
0.0	31.82	
-0.1	33.79	
-0.2	35.36	
-0.3	33.69	
-0.4	23.96	
-0.5	15.69	29.08
-0.53	14.15	
-0.56	12.88	0.85
		$Q(T) = 31.39$

come if the system remains in the potential valley; a similar rotation by any other path will naturally involve a higher barrier.

The next problem is to find the partition function for the molecule, treated as a rigid rotator, near the adsorbing surface. The Hamiltonian H is given by

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

where $U(z, \theta)$ is given by (3) or by Fig. 1. Since the exact quantum mechanical determination of the energy levels for a molecule with this Hamiltonian is out of the question, at least for the present, Hill's suggestion of the use of the Pitzer-Gwinn approximation¹² is resorted to:

$$f = f_{\text{classical}} \frac{f_{\text{HO quantum}}}{f_{\text{HO classical}}},$$

where

$$f_{\text{class}} = \frac{1}{h^5} \int \dots \times \int e^{-H/kT} dx dy dz d\theta d\phi dp_x dp_y dp_z dp_\theta dp_\phi,$$

and the harmonic oscillator partition functions are calculated from the shape of the potential energy surface near the minimum.

In order to calculate the harmonic oscillator expressions the normal coordinates for the oscillations must be found. $U(\alpha, \theta)$ may be expanded in a Taylor series about θ_0 and α_0 :

$$U = U_0 + [9.203(\theta - \theta_0)^2 - 47.05(\theta - \theta_0)(\alpha - \alpha_0) + 419.3(\alpha - \alpha_0)^2] \times 10^{-14} \text{ erg.} \quad (5)$$

This represents the potential energy of the system

¹² K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. 10, 428 (1942).

near U_0 , where it behaves like a harmonic oscillator. The kinetic energy for these two coordinates is given by $T = \frac{1}{2}M\dot{z}^2 + \frac{1}{2}I\dot{\theta}^2$. It may readily be shown that normal coordinates w_1 and w_2 exist such that Eq. (5) is transformed into

$$U = 2565w_1^2 + 4165800w_2^2, \quad (6)$$

where

$$w_1 + w_2 = z - z_0, \quad 10^8(-0.725w_1 + 67.28w_2) = \theta - \theta_0.$$

We are now in a position to find the harmonic oscillator partition functions. Substitution of (6) into (4) gives

$$f_{\text{HO class}} = \frac{1}{h^5} \int \cdots \int \exp \left[- \left(U_0 + 2565w_1^2 + 4165800w_2^2 + \frac{p_{w_1}^2}{2\mu_1} + \frac{p_{w_2}^2}{2\mu_2} + \frac{p_z^2 + p_v^2}{2M} + \frac{p_\phi^2}{2I \sin^2 \theta} \right) / kT \right] \times dx dy dw_1 dw_2 d\phi dp_z dp_v dp_{w_1} dp_{w_2} dp_\phi,$$

where μ is the appropriate reduced mass. Integration leads to

$$f_{\text{HO class}} = \frac{2\pi M k T}{h^2} \alpha \frac{2\pi(2\pi I k T)^{\frac{1}{2}}}{h} \times \frac{kT}{h\nu_{w_1}} \frac{kT}{h\nu_{w_2}} \exp(-U_0/kT), \quad (7)$$

where $\nu_{w_1} = 7.781 \times 10^{11}$ /sec. and $\nu_{w_2} = 3.288 \times 10^{12}$ /sec. and α is the surface area of the adsorbent. Since the variables have been separated, we may write

$$f_{\text{HO QM}} = \frac{2\pi M k T}{h^2} \alpha \frac{2\pi(2\pi I k T)^{\frac{1}{2}}}{h} \times [1 - \exp(-h\nu_{w_1}/kT)]^{-1} [1 - \exp(-h\nu_{w_2}/kT)]^{-1} \times \exp(-U_0/kT).$$

The problem is then to find f_{class} . Following the method of Hill¹ we arrive at

$$f_{\text{class}} = \left(\frac{2\pi M k T}{h^2} \right)^{\frac{1}{2}} \alpha \frac{8\pi^2 I k T}{h^2} \frac{r_0 \text{ CH } r_0 \text{ CI}}{0.992d} \times \int \int \exp(-U/kT) \text{erf}(-U/kT)^{\frac{1}{2}} d\alpha d\beta, \\ -0.560 \cos \theta \leq \beta \leq +0.560 \cos \theta, U \leq 0. \quad (8)$$

Because of the nature of U , which is given by (3), this integration must be carried out numerically.

β is held constant while α is integrated, by means of Simpson's rule, from the value of α such that $U=0$ to a sufficiently large value of α ; beyond here the integral is evaluated analytically, using asymptotic expressions, to $\alpha = \infty$. These results are then integrated from $\beta = -0.560 \cos \theta$ to $\beta = 0.560 \cos \theta$. Calculations for two temperatures (81.33°K and 244°K) have been carried out. The results are given in Tables II and III. Let $Q(T)$ be the result of the second integration for temperature T .

The final results for f_{class} are

$$f_{\text{class}} = \left(\frac{2\pi M k T}{h^2} \right)^{\frac{1}{2}} \alpha \frac{8\pi^2 I k T}{h^2} \frac{r_0 \text{ CH } r_0 \text{ CI}}{0.992d} Q(T).$$

When substituted into (4), these lead to

$$f = \rho_1 \rho_2 j_{\text{el}} j_{\text{vib}} \alpha \left(\frac{2\pi M k T}{h^2} \right)^{\frac{1}{2}} \frac{8\pi^2 I k T}{h^2} \frac{r_0 \text{ CH } r_0 \text{ CI}}{0.992d} Q(T) \times \frac{h\nu_{w_1}}{kT} \frac{h\nu_{w_2}}{kT} [1 - \exp(-h\nu_{w_1}/kT)]^{-1} \times [1 - \exp(-h\nu_{w_2}/kT)]^{-1}. \quad (9)$$

Here ρ_i is the nuclear spin of atom i of the adsorbed molecule, and j_{el} and j_{vib} are the electronic and internal vibrational partition functions, respectively, for such a molecule. Inserting the proper numerical values, we find that

$$f = \rho_1 \rho_2 j_{\text{el}} j_{\text{vib}} \left(\frac{2\pi M k T}{h^2} \right)^{\frac{1}{2}} \alpha \frac{8\pi^2 I k T}{h^2} \times (4.181 \cdot 10^{-2}) \quad T = 81.33, \\ f = \rho_1 \rho_2 j_{\text{el}} j_{\text{vib}} \left(\frac{2\pi M k T}{h^2} \right)^{\frac{1}{2}} \alpha \frac{8\pi^2 I k T}{h^2} \times (3.070 \cdot 10^{-6}) \quad T = 244. \quad (10)$$

The BET constant C may be written in the form $C = R \exp(\epsilon_1 - \Lambda)/kT$. If we consider adsorption at very low pressures, so that the adsorbed molecules do not interact with each other to any appreciable extent, we can arrive¹ at the expression

$$C = \frac{f}{N^0} \frac{p_0}{kT} \left(\frac{h^2}{2\pi M k T} \right)^{\frac{1}{2}} \left(\frac{h^2}{8\pi^2 I k T} \right) \frac{1}{\rho_1 \rho_2 j_{\text{el}} j_{\text{vib}}},$$

where N^0 is the maximum number of molecules that can be adsorbed in the first layer, and p_0 is the vapor pressure, at the temperature T , of the gas being adsorbed. Since p_0 may be written¹ as $\delta \exp(-NkT)$, and since we have already found 1.710×10^{-13} erg per molecule for ϵ_1 ,

$$R = 1.027 \times 10^{-8} (\alpha/N^0) (\delta/kT) \quad T = 81.33, \quad (11) \\ R = 1.919 \times 10^{-8} (\alpha/N^0) (\delta/kT) \quad T = 244.$$

Use of the values $\Lambda = 4332$ calories per mole and $p_0 = 713.1$ mm of mercury for hydrogen iodide at 236.1°K leads to the result $\delta = 9.784 \times 10^9$. α/N^0 , the area occupied per molecule adsorbed in a completed first layer, may be calculated¹ from

$$\alpha/N^0 = 6.354(T_c/P_c)^{1/2},$$

where T_c and P_c are the critical temperature and pressure, respectively. If T_c is taken as 424.2°K and P_c as 82 atmospheres, $\alpha/N^0 = 19.00$ sq. A.

Substitution of these values into (11) leads to $R = 10.58$ at 244°K and to $R = 16.99$ at 81.33°K . These R values are of the same order of magnitude as those found by Hill for the symmetrical diatomic molecule. It is of interest to note that in this case R is roughly proportional to T^{-1} .

Actually, of course, at 81.33°K there is a good possibility of localized adsorption, so the value of R_{loc} (localized) should also be found. We employ Eqs. (35) and (36) in reference 1. Assuming that for graphite the potential barriers lie at the centers of hexagons, we get for s , the barrier spacing, 2.46\AA . If V_0 , the height of the barrier, is then taken as 1000 calories per mole, which is probably a rather high value, the frequency of vibration parallel to the surface is 3.68×10^{11} per second, and R_{loc} becomes $0.127R = 2.16$.

III. CASE B: SIMULATED BENZENE

Another type of molecule for which calculations of this sort may be of interest is the ring molecule. Benzene is probably the most important example of this type, and it is with this molecule we deal specifically, but a similar treatment should be applicable to certain other organic molecules.

Since benzene contains twelve atoms, calculations of the energy of adsorption by summing the interaction energies of each atom with the surface would be extremely laborious, at best. The molecule to be adsorbed is therefore temporarily taken to be in the form of two coplanar, concentric, circular rings, one of carbon and one of hydrogen. In each ring, the mass is assumed to be continuous and uniformly distributed around the circumference, with the total mass of the ring equal to the sum of the corresponding atomic masses. The molecule is regarded as rigid, so that the radius and mass distribution of each ring remains constant.

Let us consider a single circular ring or loop whose center is at a distance z_0 from a uniform surface which is represented by the xy plane; let the z axis pass through the center of the loop. Let the radius of the ring be d . Let a line be drawn through the center of the loop and perpendicular to its plane; this line makes an angle θ with the z axis, corresponding to the θ in case A.

The interaction of a mass point on this ring with

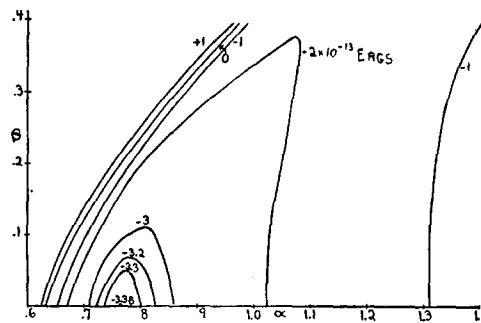


FIG. 2.

the surface will be again represented by

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

The interaction of the entire loop with the surface will be found by integration of this equation around the loop. For a ring of n atoms, we find

$$U = -\frac{n}{\pi} \left\{ \frac{\pi u_0 r_0^{12} N_0}{45} \frac{\pi}{128} \times \left[\frac{128a^8 + 1792a^6b^2 + 3360a^4b^4 + 1120a^2b^6 + 35b^8}{(a^2 - b^2)^{17/2}} \right] - \frac{\pi u_0 r_0^6 N_0}{3} \left[\frac{2a^2 + b^2}{(a^2 - b^2)^{5/2}} \right] \right\}$$

where $a = z_0$ and $b = d \sin \theta$.

The benzene might now be approximated by a ring of six carbon atoms. It would also be possible to use (12) for the carbon and hydrogen rings separately, and add the results. However, the most practical course seems to be to postulate a hypothetical ring of six "C—H" atoms such that the interaction of each member of the ring with the graphite surface is given by

$$u_{\text{HC-C}} = u_0 \text{HC-C} \left(\frac{r_0 \text{HC-C}}{r} \right)^{12} - 2u_0 \text{HC-C} \left(\frac{r_0 \text{HC-C}}{r} \right)^6. \quad (1A)$$

The values for $r_0 \text{HC-C}$ and $u_0 \text{HC-C}$ are approximated as follows. In the more complete interaction equation

$$u_0 \text{HC-C} = u_0 \text{HC} \left(\frac{r_0 \text{HC}}{r} \right)^{12} - 2u_0 \text{HC} \left(\frac{r_0 \text{HC}}{r} \right)^6 + u_0 \text{CC} \left(\frac{r_0 \text{CC}}{r} \right)^{12} - 2u_0 \text{CC} \left(\frac{r_0 \text{CC}}{r} \right)^6 \quad (1B)$$

the values $u_{0\text{CC}} = 6.60 \times 10^{-15}$ erg, $u_{0\text{HC}} = 3.687 \times 10^{-15}$ erg, $r_{0\text{HC}} = 2.87\text{\AA}$, and $r_{0\text{CC}} = 3.34\text{\AA}$ are substituted; these values are those obtained from Table I. Equation (1B) is differentiated with respect to r . Then, setting $du/dr = 0$, a condition which holds at the position of minimum u , we solve for r and find that $r = 3.281\text{\AA}$. This value is taken to be $r_{0\text{HC-C}}$; it is now substituted for r in Eq. (1B), and the resulting $u = 9.078 \times 10^{-15}$ erg is considered to be $u_{0\text{HC-C}}$.

The radius of the carbon "ring" in benzene is

TABLE IV. Integration for C_6H_6 at 273°K .

β	$f(\beta)$	$\frac{\beta}{[(d/r_0)^2 - \beta^2]^{\frac{1}{2}}}$	$\frac{f(\beta)\beta}{[(d/r_0)^2 - \beta^2]^{\frac{1}{2}}}$	$\int \frac{f(\beta)\beta d\beta}{[(d/r_0)^2 - \beta^2]^{\frac{1}{2}}}$
0.0	1108.43	0	0	
0.05	836.56	0.172	143.80	
0.1	483.56	0.353	170.70	12.43
0.2	153.38	0.790	123.48	
0.3	65.71	1.476	96.97	
0.4	36.30	3.000	108.90	
0.5	24.03	15.473	371.82	55.53
0.54	21.76			4.68
0.6	18.35			
$Q = 72.64$				

1.39 \AA ; the radius of the surrounding hydrogen loop⁹ is 2.47 \AA . In selecting a value for d , the radius of the hypothetical C—H ring, it seems desirable to weight these radii in accordance with their interaction energies with graphite. For this reason, d is taken to be

$$1.39 + \frac{u_{0\text{HC}}}{u_{0\text{HC}} + u_{0\text{CC}}} (2.47 - 1.39) = 1.78\text{\AA}.$$

(For convenience, $r_{0\text{HC-C}}$ will henceforth be denoted by r_0 and $u_{0\text{HC-C}}$ by u_0 .)

Using $n = 6$, Eq. (12) becomes

$$U = \frac{A}{960} \left[\frac{128\alpha^8 + 1792\alpha^6\beta^2 + 3360\alpha^4\beta^4 + 1120\alpha^2\beta^6 + 35\beta^8}{(\alpha^2 - \beta^2)^{17/2}} - A \left[\frac{2\alpha^2 + \beta^2}{(\alpha^2 - \beta^2)^{5/2}} \right], \quad (13) \right.$$

where $\alpha = a/r_0$, $\beta = b/r_0$, and $A = \pi r_0^3 u_0 N_0 = 1.136 \times 10^{-13}$ erg per molecule.

Equation (13) is now used to find $U(\alpha, \beta)$. The results are shown graphically in Fig. 2. The plot, as expected, is symmetrical about the line $\beta = 0$. The position of minimum energy is determined, as before, by the conditions $\partial U/\partial \alpha = 0$ and $\partial U/\partial \beta = 0$; it occurs at $\beta = 0$, $\alpha = 0.7647r_0$ in analogy with the monatomic case. The potential energy of the system at this point, U_0 , is -3.388×10^{-13} erg per

molecule (4875 calories per mole). As β increases, and the molecule tilts relative to the surface, the center of mass of the molecule is found to move away from the surface in order to be in the position of least potential energy. This motion results naturally from the fact that, as r decreases, the repulsive term increases more rapidly than the attractive one. For the molecule to flip over, it must overcome a potential barrier of approximately 3400 calories per mole, if it follows the path of least resistance.

To find the partition function for this molecule considered as a rigid rotator, we write its Hamiltonian

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2M} + \frac{p_\phi^2}{2A} + \frac{(p_\psi - \cos\theta p_\psi)^2}{2A \sin^2\theta} + \frac{p_\psi^2}{2C} + U(z, \theta), \quad (14)$$

where A is the moment of inertia of the molecule about a diameter; C is the moment about an axis perpendicular to the loop and through its center; $U(z, \theta)$ is given by (13); and ϕ , θ , and ψ are the normal Eulerian angles.¹³

Since the quantum mechanical problem for a rotator with this Hamiltonian is unsolved, the Pitzer-Gwinn approximation is again resorted to. Near the point ($\alpha = \alpha_0$, $\beta = \beta_0$), $U(\alpha, \beta)$ may be expanded in a Taylor's series:

$$U = -3.388 \times 10^{-13} + 3.911 \times 10^{-12} (\alpha - \alpha_0)^2 + 7.822 \times 10^{-12} (\beta - \beta_0)^2. \quad (15)$$

The partition function $f_{\text{HO class}}$ may then be found by the integration of

$$f_{\text{HO class}} = \frac{1}{h^6} \int \cdots \int \exp \left[-U_0 + \frac{c_1}{r_0^2} (z_0 - z_{00})^2 + \frac{c_2}{r_0^2} d^2 (\sin\theta - \sin\theta_0)^2 + \frac{p_x^2 + p_y^2 + p_z^2}{2M} + \frac{p_\phi^2}{2A} + \frac{(p_\psi - \cos\theta p_\psi)^2}{2A \sin^2\theta} + \frac{p_\psi^2}{2C} \right] / kT \\ \times dx dy dz_0 d\theta d\phi d\psi dp_x dp_y dp_z dp_\phi dp_\psi dp_\psi.$$

Here c_1 and c_2 are the respective coefficients of the square terms in (15), and $z_{00} (= \alpha_0 r_0)$ is the value of z_0 for which U is a minimum. The limits of integration are 0 to π for θ , 0 to 2π for ϕ and ψ , the limits of the surface for x and y , and $-\infty$ to $+\infty$ for the other variables. In our case, $\theta_0 = 0$, so

¹³ Equation (14) is equivalent to Eq. (8.9) in Mayer and Mayer's *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

$\sin\theta_0=0$. Furthermore, since we are interested only in oscillations very near the minimum, we may make the approximation that $\sin\theta=\theta$. If then it is assumed that

$$\int_0^\pi e^{-a\theta^2}\theta d\theta = \int_0^\infty e^{-a\theta^2}\theta d\theta,$$

the result is

$$f_{\text{HO class}} = 4\pi^2 \alpha \frac{r_0^3 kT}{2c_2 d^2} \left(\frac{\pi kT}{c_1}\right)^{\frac{1}{2}} \left(\frac{2\pi M kT}{h^2}\right)^{\frac{1}{2}} \times \left(\frac{2\pi A kT}{h^2}\right) \frac{(2\pi C kT)^{\frac{1}{2}}}{h} \exp(-U_0/kT).$$

For a harmonic oscillator subject to (15)

$$\nu_{z_0} = \frac{1}{\pi r_0} \left(\frac{c_1}{2M}\right)^{\frac{1}{2}} = 1.69 \times 10^{12}$$

$$\text{and } \nu_\theta = \frac{d}{\pi r_0} \left(\frac{c_2}{2A}\right)^{\frac{1}{2}} = 2.38 \times 10^{12}/\text{sec}.$$

The above may then be written

$$f_{\text{HO class}} = \alpha \frac{2\pi M kT}{h^2} 2\pi \frac{(2\pi C kT)^{\frac{1}{2}}}{h} \times \frac{kT}{h\nu_{z_0}} \left(\frac{kT}{h\nu_\theta}\right)^2 \exp(-U_0/kT). \quad (16)$$

Making the usual assumptions about the definition of an adsorbed molecule, one arrives at the result

$$f_{\text{class}} = 4\pi^2 \alpha \left(\frac{2\pi M kT}{h^2}\right)^{\frac{1}{2}} \left(\frac{2\pi A kT}{h^2}\right) \frac{(2\pi C kT)^{\frac{1}{2}}}{h} \times 2 \int_{\substack{0 \leq \theta \leq \pi/2 \\ U \leq 0}} \exp(-U/kT) \text{erf}(-U/kT)^{\frac{1}{2}} \sin\theta d\theta dz_0.$$

Upon substitution of $d\alpha=dz/r_0$, $\sin\theta=\beta r_0/d$, and

$d\theta=r_0 d\beta/d \cos\theta$, there results

$$f_{\text{class}} = 4\pi^2 \alpha \left(\frac{2\pi M kT}{h^2}\right)^{\frac{1}{2}} \left(\frac{2\pi A kT}{h^2}\right) \frac{(2\pi C kT)^{\frac{1}{2}}}{h} \times \frac{2r_0^2}{d} \int_0^{d/r_0} \frac{\beta d\beta}{[(d^2/r_0^2)-\beta^2]^{\frac{1}{2}}} \times \int_{U \leq 0} \exp(-U/kT) \text{erf}(-U/kT)^{\frac{1}{2}} d\alpha. \quad (17)$$

The integral in (17) may be evaluated numerically. The integration is first performed over all those values of α such that U is negative (out to some α beyond which the integral may be evaluated analytically by the use of asymptotic expressions), and then over β . The results are given in Table IV; Q , the result of the final integration, = 72.64, if the temperature is taken to be 273°K.

Use of Eq. (4) yields

$$f = f_{\text{class}} \frac{\rho^2}{\sigma} j_{\text{el},j_{\text{vib}}} \left(\frac{h\nu_{z_0}}{kT}\right) \left(\frac{h\nu_\theta}{kT}\right)^2 \left[1 - \exp\left(-\frac{h\nu_{z_0}}{kT}\right)\right]^{-1} \left[1 - \exp\left(-\frac{h\nu_\theta}{kT}\right)\right]^{-2}, \quad (18)$$

where σ is the symmetry number of the adsorbed molecule. Following the method used in case A, we find

$$R = Q \frac{\alpha}{N^0} \frac{r_0^2}{d} \frac{\delta}{kT} \exp(-U_0/kT) \nu^{**},$$

where ν^{**} is the product of the frequency factors in (18). α/N^0 , the area occupied per molecule adsorbed in a completed first layer, is calculated by $\alpha/N^0 = 6.354(T_c/P_c)^{\frac{1}{2}}$; using $T_c = 561.7^\circ\text{K}$ and $P_c = 47.7$ atmospheres, gives 32.89 sq. A. If the latent heat of vaporization of benzene is taken to be 447.8 joules per gram at 273°K, and the corresponding vapor pressure is 26.54 mm of mercury, use of the equation $p_0 = \delta \exp(-\Lambda/kT)$ gives the result that δ for benzene is 1.717×10^{11} .

Employing these values, we find that R for mobile adsorption is 14.27. This is of the same order of magnitude as the results found for previous cases. The classical result, which is found by employing f_{class} instead of f , differs only by the product of the frequency factors. Since this is 1.731, we find $R_{\text{class}} = R/1.731 = 8.245$.