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Significant Structure Theory of Physical Adsorption

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Abstract A significant structure theory of monolayer physical adsorption is developed. The theory is tested with the adsorptions on graphite of gases Ar, N_2, $CHCl_3$, and CCl_4. A restricted rotation model is used for the polyatomic molecules N_2, $CHCl_3$ and CCl_4. The computed isotherms and heats of adsorption are in good agreement with experiment in all cases studied.

Introduction

In a previous paper[1], we showed that the significant structure theory of liquids was successfully applied to a two-dimensional liquid of hard discs. A further extention of the investigation is to show how the theory can describe the physical adsorption of gases on solids. In this paper only a theory of monolayer adsorption on homogeneous surfaces will be discussed. For a basic understanding of the significant structure theory, the readers are referred to the literature[2] and the references cited therein.

Theory

According to the significant structure theory, the partition function for the adsorbed state is given by[3]

$$f_{ads}=\left[f_{2s}\left(1+n_h e^{-\frac{\varepsilon_0}{RT}}\right)\right]^{N'\frac{A_S}{A}}\left[f_{2g}\right]^{N'\left(1-\frac{A_S}{A}\right)} \tag{1}$$

where f_{2s} is the partition function for the two-dimensional solid-like structure, f_{2g} the partition function for the two-dimensional gas-like structure, N' the number of adsorbed molecules, A_S the molar area of the two-dimensional solid-like structure, and A the molar area of the adsorbed state. Let θ be the fraction of the surface covered with adsorbed molecules, N_m be the number of adsorbed molecules when $\theta=1$, and A_m be the molar area of the adsorbed molecule at $\theta=1$. We then find that $A=A_m/\theta$ and $N'=N_m\theta$. Eq. (1) becomes,

$$f_{ads}=\left[f_{2s}\left(1+n_h e^{-\frac{\varepsilon_0}{RT}}\right)\right]^{N_m-\frac{A_S}{A_m}\theta}\left[f_{2g}\right]^{N_m\left(1-\frac{A_S}{A_m}\theta\right)\theta} \tag{2}$$

The quantity $(1+n_h \exp(-\varepsilon_0/RT))$ in Eq. (2) is the positional degeneracy for a solid-like molecule. The number of vacancies around a solid-like molecule, n_h, is given by[2]

$$n_h=Z\frac{A-A_S}{A}=Z\left(1-\frac{A_S}{A_m}\theta\right) \tag{3}$$

where Z is the coordination number 6.

The energy ε_0 associated with the positional degeneracy should be inversely proportional to the number of vacancies and directly proportional to the configurational energy of the two-dimensional solid-like structure, which is the sum of the adsorbate-adsorbate interaction energy W and the adsorbate-adsorbent interaction energy U_0. Therefore, we write,

$$\varepsilon_0=a\frac{W+U_0}{(A-A_S)/A_S}=a(W+U_0)\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta} \tag{4}$$

where a is a proportionality constant. For f_{2s} and f_{2g} we can use the following expressions:

$$f_{2s}=\frac{e^{-h\nu_\perp/2kT}}{1-e^{-h\nu_\perp/kT}}e^{U_0/RT}\left(\frac{e^{-h\nu_{//}/2kT}}{1-e^{-h\nu_{//}/kT}}\right)^2 e^{W/RT}J_{2s} \tag{5}$$

$$f_{2g}=\frac{e^{-h\nu_\perp/2kT}}{1-e^{-h\nu_\perp/kT}}e^{U_0/RT}\frac{2\pi mkT}{h^2}\frac{eA_m}{\theta N}J_{2g} \tag{6}$$

where N is Avogadro's number, $\nu_\perp$ is the frequency of the vibration normal to the surface, $\nu_{//}$ is the frequency of the vibration parallel to the surface, and J_{2s} and J_{2g} are the partition functions for all the remaining degrees of freedom other than those explicitly specified for the two-dimensional solid-like structure and the two-dimensional gas-like structure, respectively. Also A_m/θ is used in place of A in Eq. (6). Using Eqs. (3) through (6), Eq. (2) finally becomes,

$$f_{ads}=\left\{\left(2\sinh\frac{h\nu_\perp}{2kT}\right)^{-1}e^{U_0/RT}\left(2\sinh\frac{h\nu_{//}}{2kT}\right)^{-2}e^{W/RT}J_{2s}\right.$$
$$\left.\left[1+Z\left(1-\frac{A_S}{A_m}\theta\right)\exp\left(-a\frac{W+U_0}{RT}\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)\right]\right\}^{N_m-\frac{A_S}{A_m}\theta}$$
$$\times\left\{\left(2\sinh\frac{h\nu_\perp}{2kT}\right)^{-1}e^{U_0/RT}\frac{2\pi mkT}{h^2}\frac{eA_m}{\theta N}J_{2g}\right\}^{N_m\theta\left(1-\frac{A_S}{A_m}\theta\right)} \tag{7}$$

The chemical potential of the adsorbed state μ_{ads} is

$$\frac{\mu_{ads}}{kT}=-2\frac{A_S}{A_m}\theta\left\{\ln\frac{\left(2\sinh\frac{h\nu_{//}}{2kT}\right)^{-2}e^{W/RT}J_{2s}}{\left(\frac{2\pi mkT}{h^2}\frac{eA_m}{\theta N}\right)J_{2g}}\left[1+Z\left(1-\frac{A_S}{A_m}\theta\right)\exp\left(-a\frac{W+U_0}{RT}\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)\right]\right\}$$

$$-\ln\left\{\left(2\sinh\frac{h\nu_{\perp}}{2kT}\right)^{-1}e^{U_0/RT}\frac{2\pi mkT}{h^2}\ \frac{eA_m}{\theta N}J_{2s}\right\}+\left(1-\frac{A_S}{A_m}\theta\ \right)$$

$$+\frac{Z\left(\frac{A_S}{A_m}\theta\right)^2\exp\left(-a\frac{W+U_0}{RT}\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)\left(1+a\frac{W+U_0}{RT}\frac{1}{1-(A_S/A_m)\theta}\right)}{1+Z\left(1-\frac{A_S}{A_m}\theta\right)\exp\left(-a\frac{W+U_0}{RT}\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)} \tag{8}$$

since

$$\frac{\mu_{ads}}{kT}=-\left[\frac{\partial\ln f_{ads}}{\partial N'}\right]_{A,T}=\frac{-1}{N_m}\left[\frac{\partial\ln f_{ads}}{\partial\theta}\right]_{A_m,T} \tag{9}$$

The chemical potential μ_{gas} of the three dimensional gaseous state which is assumed to be ideal is

$$\frac{\mu_{gas}}{kT}=-\ln\left[\frac{(2\pi mkT)^{3/2}}{h^3}(kT)J_{gas}\right]+\ln P \tag{10}$$

where J_{gas} is the partition function for all the remaining degrees of freedom other than the three translational degrees of freedom for the gaseous state. Equating the two chemical potentials yields the isotherm equation,

$$\ln P=\ln\left\{\frac{(2\pi mkT)^{3/2}}{h^3}(kT)\,J_{gas}\right\}-\ln\left\{\left(2\sinh\frac{h\nu_{\perp}}{2kT}\right)^{-1}e^{U_0/RT}\frac{2\pi mkT}{h^2}\ \frac{eA_m}{\theta N}J_{2s}\right\}$$

$$-2\frac{A_S}{A_m}\theta\ln\left\{\frac{\left(2\sinh\frac{h\nu_{//}}{2kT}\right)^{-2}e^{W/RT}J_{2s}}{\left(\frac{2\pi mkT}{h^2}\ \frac{eA_m}{\theta N}\right)J_{2s}}\left\{1+Z\left(1-\frac{A_S}{A_m}\theta\right)\exp\left(-a\frac{W+U_0}{RT}\right)\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)\right\}\right\}$$

$$+\left(1-\frac{A_S}{A_m}\theta\right)+\frac{Z\left(\frac{A_S}{A_m}\theta\right)^2\exp\left(-a\frac{W+U_0}{RT}\ \frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)\left(1+a\frac{W+U_0}{RT}\ \frac{1}{1-(A_S/A_m)\theta}\right)}{1+Z\left(1-\frac{A_S}{A_m}\theta\ \right)\exp\left(-a\frac{W+U_0}{RT}\ \frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)} \tag{11}$$

The isosteric heat of adsorption can be obtained by the following relation,

$$q_{st}(\theta,T)=RT^2\left(\frac{\partial\ln P}{\partial T}\right)_{\theta} \tag{12}$$

Since we are developing a theory of monolayer adsorption, and since in reality multilayer adsorption will begin to start before the completion of the monolayer, any monolayer theory is not expected to hold at very high coverage. Therefore, we neglect terms involving θ of higher powers than one in the expression for the isosteric heat of adsorption. These higher order terms will not contribute appreciably to the isosteric heat of adsorption over a low coverage range where the monolayer adsorption theory is exactly applicable. The isosteric heat of adsorption is then given by

$$q_{st}(\theta,T)=RT^2\left\{\frac{3}{2T}+\frac{\partial}{\partial T}\ln\left(\frac{J_{gas}}{J_{2s}}\right)+\frac{U_0}{RT^2}-\frac{h\nu_{\perp}}{2kT^2}\coth\frac{h\nu_{\perp}}{2kT}\right.$$

$$\left.+2\frac{A_s}{A_m}\theta\left[\frac{W}{RT^2}+\frac{1}{T}-\frac{h\nu_{//}}{kT^2}\coth\frac{h\nu_{//}}{2kT}-\frac{\partial}{\partial T}\ln\left(\frac{J_{2t}}{J_{2s}}\right)\right]\right\} \tag{13}$$

Calculations

At least in our present case where a mobile layer adsorbed on an ideal homogeneous surface is considered, it seems reasonable and is commonly assumed that the adsorbed state upon completion of the monolayer has the density of the liquid state[4,5]. Thus the molar area of the adsorbed state at $\theta=1$ can be estimated by the following equation[5],

$$A_m/N=3.464\left(\frac{M}{4\sqrt{2}N\delta}\right)^{2/3} \tag{14}$$

where M is the molecular weight, N is Avogadro's number, and δ is the density of the liquid at a given temperature. It follows then that A_m is proportional to $V^{2/3}$, V being the molar liquid volume. Therefore, when isotherms of widely different temperatures are considered, a proper correction of A_m (or N_m) is necessary. However, over a moderate temperature range such a correction can generally be ignored. In this study the correction for N_m has generally improved the results. The molar area A_S of the solid-like structure is also calculated from Eq. (14), using the solid density at the melting point instead of the liquid density.

Ree et al.[6] demonstrated that for simple liquids the Einstein characteristic temperature θ_E and the sublimation energy E_S required in the significant structure theory could be calculated using the 6-12 Lennard-Jones potential. The frequency $\nu_{//}$ and the adsorbate-adsorbate interaction energy W in our formulations can also be obtained in an analogous manner. Assuming a hexagonal packing and a 6-12 Lennard-Jones type of intermolecular potential for the two-dimensional solid-like structure, we can evaluate the adsorbate-adsorbate interaction W by summing up the pairwise interaction over the 18 nearest neighbors and integrating over the rest of the two-dimensional hexagonal lattice (cf. Appendix):

$$W=\frac{ZN}{2}\varepsilon\left[2.1431\left(\frac{r_0}{r}\right)^6-1.0016\left(\frac{r_0}{r}\right)^{12}\right] \tag{15a}$$

where ε and r_0 are the Lennard-Jones potential parameters characteristic of the molecule. According to Ree et al.[6] the sublimation energy E_S of a close packed solid is given by,

$$E_S=\frac{ZN}{2}\varepsilon\left[2.4090\left(\frac{r_0}{r}\right)^6-1.0109\left(\frac{r_0}{r}\right)^{12}\right] \tag{15b}$$

Thus, at $r=r_0$ we obtain the relation:

$$\frac{W}{E_S}=\frac{6(2.1431-1.0016)}{12(2.4090-1.0109)}=0.408 \tag{16}$$

Consequently, in the following calculations we shall choose the value of W such that

$$W=0.408\ (E_S)_{exp} \tag{17}$$

where $(E_S)_{exp}$ is the experimental energy of sublimation.

For simplicity, we neglect the interaction with all molecules except the nearest six in the first shell of the hexagonal lattice in the evaluation of the Einstein characteristic temperature of the two-dimensional solid-like structure. The averaged potential due to the six neighbors is given by[7]

$$6[\Phi(r)-\Phi(\sigma)]=6\varepsilon\left[\left(\frac{r_0}{r_1}\right)^{12}\left(\frac{1+12y+\cdots}{(1-y)^{10}}-1\right)-2\left(\frac{r_0}{r_1}\right)^6\left(\frac{1+y}{(1-y)^4}-1\right)\right] \tag{18}$$

where r_1 is the distance between two neighboring molecules (*i. e.*, two neighboring cells), which equals $(\sqrt{2}V_S/N)^{1/3}$, for close packing,

$y=(r/r_0)^2$, and $\Phi(r)$ and $\Phi(o)$ are the averaged potentials at a distance r from the cell center and at the cell center, respectively. Expanding Eq. (18) in a power series of y and preserving only the first power term of y, we obtain

$$6[\phi(r)-\phi(o)]=\frac{6\varepsilon}{r_0^2}\left[22\left(\frac{r_0}{r_1}\right)^{12}-10\left(\frac{r_0}{r_1}\right)^{6}\right]r^2 \tag{19}$$

Then the force constant of the harmonic oscillation is

$$k_r=\frac{12\varepsilon}{r_0^2}\left[22\left(\frac{r_0}{r_1}\right)^{12}-10\left(\frac{r_0}{r_1}\right)^{6}\right] \tag{20}$$

since

$$6[\Phi(r)-\Phi(o)]=\frac{1}{2}k_r r^2 \tag{21a}$$

Ree et al.[6] expressed the force constant k_r for a three dimensional interaction by

$$k_r=\frac{24\varepsilon}{r_0^2}\left[22\left(\frac{r_0}{r_1}\right)^{12}-10\left(\frac{r_0}{r_1}\right)^{6}\right] \tag{21b}$$

A comparison of Eq. (20) with Eq. (21b) leads to the approximation

$$k_r=2k_r$$

Since the square root of the force constant is proportional to the vibrational frequency, one obtains the relation,

$$\nu_H=\frac{k}{h}\frac{(\theta_E)_{exp}}{\sqrt{2}} \tag{22}$$

where $(\theta_E)_{exp}$ is the experimental Einstein characteristic temperature of the solid.

It seems advisable at this stage to adopt a universal value for the dimensionless quantity a. By so doing, we eliminate some arbitrariness without affecting our results appreciably. A universal value for a has been recommended in the application of the significant structure theory to liquids[8]. All the following calculations are based on the value of $a=0.0052$, which is the value found for liquid argon.

There has not yet been a successful a priori calculation of the adsorption potentials U_0 nor of the frequency ν_H. The estimation of U_0 from the heat of adsorption is still the best procedure, but it invariably involves assuming a model for the adsorbed state. We shall choose our values of adsorption potentials so that the best fits of the adsorption heats at $\theta=0$ and the isotherms are achieved. In *Table I* the values of U_0 so chosen and W and ν_H calculated from Eqs. (17) and (22), respectively, are tabulated along with other molecular properties predetermined.

We first apply our theory to the adsorption of argon on graphite surfaces. The partition function for adsorbed argon is obtained from Eq. (7) by equating J_{2s} and J_{2g} to unity. The isotherms and heats of adsorption are, respectively, obtained from Eqs. (11) and (13) using the adsorption properties given in *Table I*. The

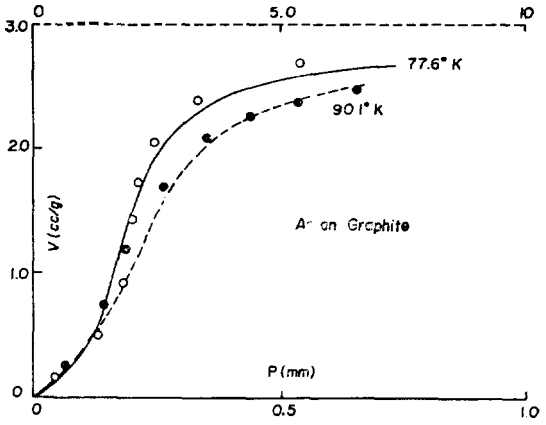

Figure 1. Adsorption isotherms of Ar on graphite P-33 at 77.6° and 90.1°K. The solid and dotted lines are theoretical. The points are experimental.[9]

results are shown in *Figures* 1 *and* 2. The close agreement with experiment[9,10] is quite evident. McAlpin and Pierotti[3] obtained similar results in their study of this system by means of the significant structure theory. However, they

Table I Molecular properties and parameters

	U_0 (cal/mole)	$\nu_\perp \times 10^{-12}$	W (cal/mole)	$\nu_{//} \times 10^{-12}$	$\frac{A_m}{N}$ (Å²/molecule)	$\frac{A_s}{N}$ (Å²/molecule)	B_0 (cal/mole)
Ar	2170	1.2[a]	771[j]	0.88[j]	13.8(77.3°K)[f] 14.4(90.1°K)[f]	13.17[h]	
N_2	2250	1.4[b]	624[j]	0.82[j]	16.2(77.3°K)[f] 17(90.1°K)[f]	14.56[h]	39
$CHCl_3$	7215	1.45[c]	2900[e]	0.84[d]	27.4(248.7°K)[g] 29.2(323.2°K)[g]	24.57[g]	160
CCl_4	7850	1.0[d]	3200[e]	0.84[j]	31.8(278.2°K)[g] 33.0(323.2°K)[g]	30.0[i]	230

a. Ref. 3.
b. S. Ross and J. P. Olivier, **On Physical Adsorption**, Interscience Publishers, 1964, p. 272.
c. Ref. 16.
d. Estimated by the authors.
e. Eq. (17) is not expected to hold for the complicated molecules. Another way of estimating W is the evaluation from the two-dimensional Van der Waal's force constants (Ref. 16).
f. D. M. Young and A. D. Crowell, **Physical Adsorption of Gases**, Butterworth, Washington, D. C., 1962.
g. International Critical Tables.
h. E. J. Fuller, T. Ree and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1594 (1959)
i. Ref. 8.
j. Calculated from Eqs. (17) and (22) by using the values of E_s and θ_E given in Refs. 2(b) and 8.

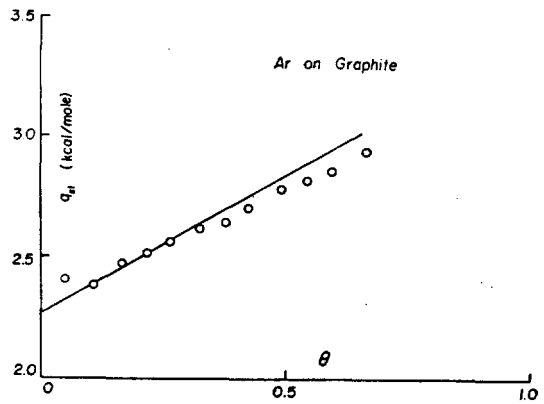

Figure 2. Isosteric heat of adsorption for Ar on graphite P-33 versus the coverage of Ar. The solid line is theoretical. The points are experimental.[10]

entirely neglected the energy ε_0 associated with the positional degeneracy and let $A_S = A_m$. It is found in the present study that these two approximations offset each other so that the final results are not noticeably affected.

In *Table II*, the isosteric adsorption heats at $\theta \simeq 0$ calculated from Eq. (13) are compared with the experimental values.[9,11] One finds good agreement.

Table II Limiting isosteric heat of adsorption on graphite (cal/mole)

	$(q_{st})_{calc.}$	$(q_{st})_{obs.}$	Remarks
Ar	2,250(at 77.6°K)	2,270	Ref. 9
N_2	2,325(at 77.6°K)	2,190	〃
$CHCl_3$	7,462(at 248.7°K)	8,000	Ref. 11
CCl_4	8,130(at 278.2°K)	8,350	〃

Adsorption of Polyatomic Gases

For many polyatomic substances a second order transition exists in the solid state. It was suggested[12] that at and beyond the transition temperature the thermal energy of the crystal surmounts the energy barrier for the intermolecular rotation, and that the intermolecular rotation begins and persists into the liquid state. Hirschfelder et al.[13] also proposed for substances without the second order transition but with unusually large entropy of fusion that the

intermolecular rotation sets in at the melting point. McLaughlin[8] improved the significant structure theory by taking into consideration the hindered intermolecular rotation in the partition functions of N_2, Cl_2, CH_4, CH_3Cl and CCl_4. In our study of adsorption of N_2, $CHCl_3$ and CCl_4 on graphite, the hindered rotation term is also incorporated. We expect that the adsorption potential U_0 of the surface will affect the rotational barrier.[14,15] The form of the rotational barrier will be very complicated even for substances of high symmetry like CCl_4. To a first approximation, we shall assume a symmetrical barrier. The fact that the rotation begins at a certain temparature (transition temperature or melting temperature) and becomes increasingly free at higher temperatures or larger volumes leads us to propose the following functional form of the rotational barrier B:

$$B=\frac{B_0}{\left(\frac{A-A_S}{A_S}\right)}=B_0\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta} \tag{23}$$

where B_0 is a constant. The partition function for the hindered rotation f_{HR} is then

$$f_{HR}=f_l+(f_{FR}-f_l)\exp\left[-\frac{B_0}{RT}\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right] \tag{24}$$

where f_l is the partition function for the "libration" into which the rotational motion will be "frozen" at low temperatures, and f_{FR} is the partition function for the free rotator. The partition function Eq. (24) is seen to satisfy the conditions that it gradually changes into that of a free rotator with increasing temperature or decreasing density and into that of a libration motion with decreasing temperature or increasing density. The frequency of the libration is usually unknown, but a reasonable approximation is to take it equal to the frequency of the vibration of the molecule normal to the surface, $\nu_\perp$. We now have only one parameter, namely B_0, to determine. The determination of B_0 is made by using the value of B_0 which best fits the adsorption isotherms. This method of determining B_0 from only one or two isotherms leaves some uncertainty. However, a value of B_0, which yields correct isotherms over a wide range of temperatures, should provide a reliable estimate of the hindering potential. The model of significant hindered intermolecular rotation for adsorption is justified by our results for such cases as N_2, $CHCl_3$ and CCl_4 on graphite.

The final forms of the J's are:

for N_2:

$$J_{2s}=\left(2\sinh\frac{h\nu_i}{2kT}\right)^{-1}\left\{\left(2\sinh\frac{h\nu_\perp}{2kT}\right)^{-2}+\left[\frac{8\pi^2IkT}{2h^2}-\left(2\sinh\frac{h\nu_\perp}{2kT}\right)^2\right]\exp\left(-\frac{B_0}{RT}\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)\right\} \tag{25}$$

$$J_{2g}=\left(2\sinh\frac{h\nu_i}{2kT}\right)^{-1}\frac{8\pi^2IkT}{2h^2} \tag{26}$$

for $CHCl_3$ and CCl_4:

$$J_{2s}=\prod_{i=1}^{6}\left(2\sinh\frac{h\nu_i}{2kT}\right)^{-1}\left\{\left(2\sinh\frac{h\nu_\perp}{2kT}\right)^{-3}+\left[\frac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}-\left(2\sinh\frac{h\nu_\perp}{2kT}\right)^{-3}\right]\exp\left(-\frac{B_0}{RT}\frac{(A_S/A_m)\theta}{1-(A_S/A_m)\theta}\right)\right\} \tag{27}$$

$$J_{2g}=\prod_{i=1}^{6}\left(\sinh\frac{h\nu_i}{2kT}\right)^{-1}\left[\frac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}\right] \tag{28}$$

Here the symmetry number σ is equal to 3 and 12 for $CHCl_3$ and CCl_4, respectively, I is the moment of inertia of nitrogen, and A, B and C are the three principal moments of inertia of the non-linear molecules. The internal vibrations of the adsorbed molecules, ν_i, are taken equal to their gaseous values.

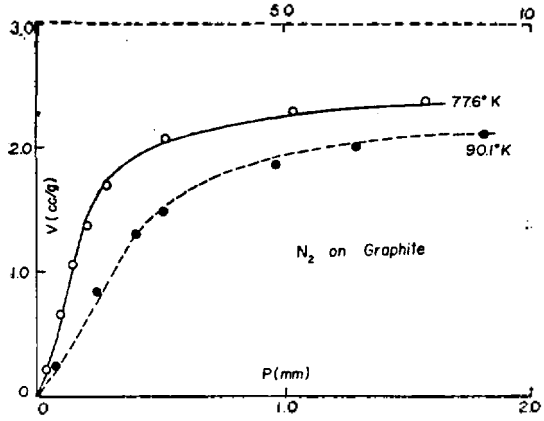

Figure 3. Adsorption isotherms of N_2 on graphite P-33 at 76.6° and 90.1°K. The solid and dotted lines are theoretical. The points are experimental.[10] The pressures for the solid and dotted curves are shown by the lower and upper scales, respectively.

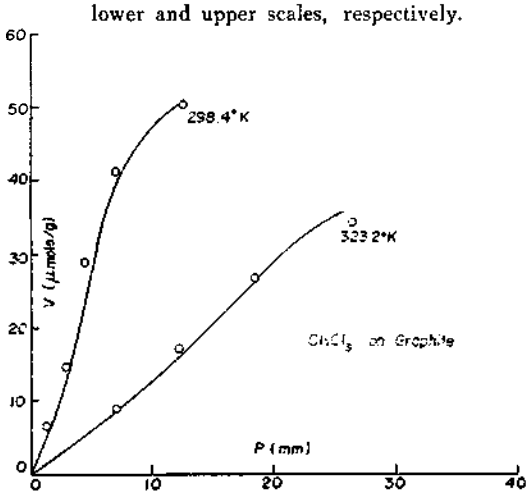

Figure 4. Adsorption isotherms of $CHCl_3$ on graphite P-33 at 323.2° and 298.4°K. The solid lines are theoretical. The points are experimental.[16]

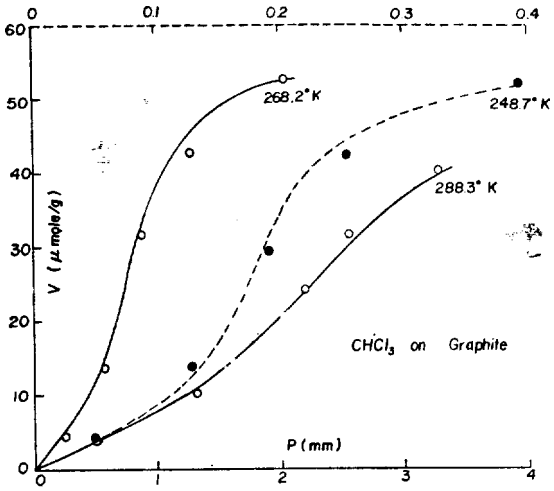

Figure 5. Adsorption isotherms of $CHCl_3$ on graphite P-33 at 248.7°, 268° and 288.3°K. The solid and dotted lines are theoretical. The points are experimental[16] The pressures for the solid and dotted curves are shown by the lower and upper scales, respectively.

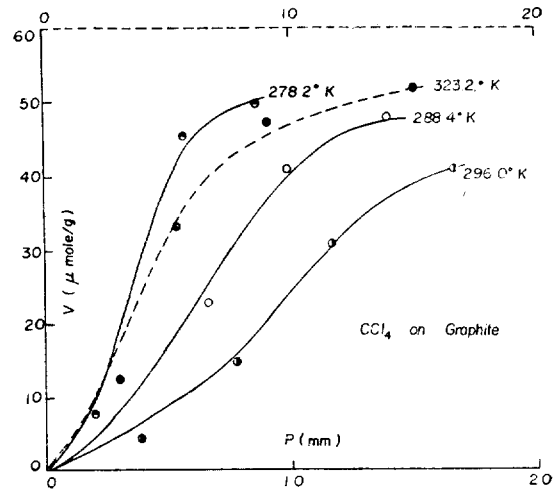

Figure 6. Adsorption isotherms of CCl_4 on graphite P-33 at 278.2°, 288.4°, 296.0° and 323° K. The solid and dotted curves are theoretical. The points are experimental.[16] The pressures for the solid and dotted curves are shown by the lower and upper scales, respectively.

Substitutions of the appropriate J's into Eqs. (7), (11) and (13) yield the partition function, the isotherm, and the isosteric heat of adsorption for the polyatomic gases, N_2, $CHCl_3$ and CCl_4.

The computed isotherms of the polyatomic gases adsorbed on graphite are shown in *Figures* 3 *to* 6. The agreement with experiment[10,16] is again very good. Particularly impressive is the correct prediction of the variation of isotherms with temperature.

Discussion

The perfect agreement of the adsorption isotherms indicates that the significant structure theory with appropriate adaptation is indeed applicable to the adsorbed state. It further indicates that the supposition of hindered rotation of the adsorbed molecules is generally correct. Of course, we should not yet attach undue significance to the values of B_0 from our oversimplified model. The B_0 is 230 cal/mole for CCl_4 adsorbed on graphite compared with 70 cal/mole for CCl_4 in the liquid state.[8] This also lends support to our assertion that the rotation is even more restricted in the adsorbed state than in the liquid state.

An ideal gas partition function has always been used for the gas-like structure in the significant structure theory. Under the influence of the potential field of the surface, the gas-like degrees of freedom of the adsorbed molecules may be considerably changed from those of the gas molecules in free space, in addition to the transformation of one degree of translational freedom of the gas molecule to one degree of vibrational freedom of the adsorbed molecule. The rotational degrees of freedom may also change. For instance, an adsorbed homo-nuclear diatomic molecule probably rotates quite freely about the axis perpendicular to the surface (with the molecular axis parallel to the surface), whereas the rotation about the axis parallel to the surface is restricted.[14,15] Therefore, we may use a different expression for J_{2s}:

$$J_{2s}=\left(2\sinh\frac{h\nu_l}{2kT}\right)^{-1}\frac{2\pi(2\pi I_r kT)^{1/2}}{2h} \tag{29}$$

instead of

$$J_{2s}=J_{2a_s}=\frac{8\pi^2 IkT}{2h^2} \tag{30}$$

where I is the moment of inertia of the diatomic molecule, I_r is the reduced moment of inertia, and ν_l is the frequency of the libration assumed to take place for the one degree of restricted rotational freedom. Similar considerations should apply for the rotational degrees of freedom of the solid-like structure.

Appendix

The Calculation of the Two-Dimensional Solid Lattice Energy We assume that the two-dimensional solid lattice is hexagonally close-packed and that the molecules interact according to the Lennard-Jones potential,

$$\phi(r)=\varepsilon[(r_0/r)^{12}-2(r_0/r)^6] \tag{1}$$

where ε and r_0 are the Lennard-Jones potential parameters of the molecules. The numer of molecules Z_i in the ith nearest shell from the molecule under consideration and the intermolecular distance to the ith shell molecules r_i are as follows.[17] For the first shell, $Z_1=6$, $r_1=r_1$; for the second shell $Z_2=6$, $r_2=\sqrt{3}r_1$; and for the third shell $Z_3=6$, $r_3=2r_1$. The total interaction with the six molecules in the first shell is,

$$W_1=6\phi(r_1)=6\varepsilon[(r_0/r_1)^{12}-2(r_0/r_1)^6] \quad (2)$$

and in general, the interaction with the ith shell molecules is,

$$W_i=Z_i\varepsilon[(r_0/r_i)^{12}-2(r_0/r_i)^6] \quad (3)$$

and the total lattice energy per molecule is

$$W=\sum_{i=1}^{\infty}(W_i/2) \quad (4)$$

We sum for the first three shells only and integrate over the remaining shells of the lattice. This gives

$$\begin{aligned}2W=&6\varepsilon[(r_0/r_1)^{12}-2(r_0/r_1)^6]\\&+6\varepsilon[(r_0/r_2)^{12}-2(r_0/r_2)^6]\\&+6\varepsilon[(r_0/r_3)^{12}-2(r_0/r_3)^6]\\&+\varepsilon\int_{r_3}^{\infty}[(r_0/r)^{12}-2(r_0/r)^6]2\pi r\left(\frac{\sqrt{3}}{2}r_1^2\right)^{-1}dr\end{aligned} \quad (5)$$

where $[(\sqrt{3}/2)r_1^2]^{-1}$ is the number of molecules per unit area. Substituting the previously given values of $r_i(r_1)$ into Eq. (5) and multiplying N one obtains

$$\begin{aligned}-W=&\frac{6\varepsilon N}{2}[1.0016\ (r_0/r_1)^{12}\\&-2.14310(r_0/r_1)^6]\end{aligned} \quad (6)$$

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