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THE THEORETICAL CALCULATION OF THE HEAT OF ADSORPTION FOR GASES PHYSICALLY ADSORBED ON CARBON SURFACES

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THE THEORETICAL CALCULATION OF THE HEAT OF ADSORPTION FOR CASES PHYSICALLY ADSORBED ON CARBON SURFACES[+]

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- Abstract -

The results of theoretical computations of the differential heat of adsorption for the low boiling gases, nitrogen, argon, neon, orthodeuterium, parahydrogen and helium (He^4), adsorbed on a graphite surface are compared with the experimental values which have been observed for these gases adsorbed on finely divided graphitic surfaces. The role of the zero point energy in the heat of adsorption is discussed. In the case of parahydrogen and orthodeuterium, the difference in the zero point energies arising from the difference in masses accounts satisfactorily for the higher heat of adsorption observed for orthodeuterium. The effect of energy barriers in the surface on the heat of adsorption is considered. For the particular case of a graphitic surface, it is shown that the energy barriers are small, and therefore, a "liquid like" behavior is reasonable for the adsorbed layers. With this behavior as a basis, an application of simple lattice-liquid theory for the characterizing of the differential heat of adsorption on a graphitic surface for surface coverage to approximately two monolayers is carried out.

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I. INTRODUCTION

Before attempting any theoretical calculation of heats of physical adsorption for various gases on carbon surfaces, it appears advisable to review the literature for the experimental values which such a calculation should reproduce. Surfaces which should be included for consideration are amorphous carbon, graphitic carbon and diamond.

Surfaces of graphite and graphitic carbon probably represent the best known carbon surfaces. This is not surprising when one considers that graphite and graphitic carbons occurring or prepared under a variety of conditions appear to possess similar lattice parameters and physical properties. Particular mention should be made of the group of graphitized carbons[1,2] which have been prepared and studied by investigators at the Godfrey L. Cabot Laboratories, Boston, Mass. It is because of the graphitization studies and adsorption studies with finely divided carbons by this group that we have our present greater understanding of the nature of graphitic surfaces. Specific mention of the nature of this work will be made in some of the following material.

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[1] M. H. Polley, W. D. Schaeffer and W. R. Smith, *J. Phys. Chem.*, *57*, 469 (1953)

[2] W. D. Schaeffer, W. R. Smith and M. H. Polley, *Ind. Eng. Chem.*, *45*, 1721 (1953)

It is unfortunate that similar statements cannot be made about amorphous carbon or diamond surfaces. The structure of amorphous carbon cannot be controlled or reproduced to the degree which is possible with graphite. Because of this, although a number of adsorption studies have been carried out, their interpretation and significance are difficult to evaluate. Diamond, in principle, should provide a well-characterized surface for adsorption but results with it are virtually non-existent.

Gases, which should be included, are the rare gases, krypton, argon, neon, helium and the diatomic gases nitrogen, oxygen and hydrogen. If some measure of success is achieved for these simple gases, extension of the treatment for more complicated molecules should be possible.

For such systems consisting of one of the molecules mentioned above adsorbed on a carbon surface, the thermodynamic quantity which is desired is either the molar differential heat of adsorption

$$\Delta H_d = \bar{H}_g - \bar{H}_{N_s} \qquad (1)$$

in which $\bar{H}_g$ = the partial molar heat content of the gas at constant pressure;

$\bar{H}_{N_s}$ = the partial molar heat content of the adsorbed phase at constant amount adsorbed,

or the isosteric heat q_{st} which is thermodynamically identical with the differential heat. Two experimental methods are available to determine the heat of adsorption defined above. The first involves the temperature coefficient of the equilibrium pressure at a constant amount adsorbed in the expression

$$\left(\frac{d \ln p}{dT}\right)_{N_s} = \frac{q_{st}}{RT^2} \tag{2}$$

and hence, the heat value is derivable from measurements of adsorption isotherms at several temperatures. The second involves the use of a calorimetric apparatus in obtaining directly the heat quantity.

Argon-graphite - Numerous studies have been carried out on this system at temperatures of 70-90°K. Barrer[3] derived values of the heat of adsorption from isotherms ranging from an initial value of 4600 cal/mole to 2400 cal/mole on a surface of Acheson graphite for which no physical data is provided. Barrer interpreted the 2400 cal/mole value as that for a graphite surface while the 4600 cal/mole value which is roughly two times this value was assumed to be the result of adsorption in cracks involving two layers of carbon atoms. Young[4,5] computed values of the isosteric heat of adsorption from the isotherm data of Jura and Griddle[6] with a sample of graphite with less than .001 percent ash, a surface area of 3.22 m^2/g and supposedly free of oxygen complexes. The values obtained range from approximately

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[3] R. M. Barrer, Proc. Roy. Soc. A 161, 476 (1937)

[4] D. H. Everett and D. M. Young, Trans. Faraday Soc., 48, 1164 (1952)

[5] A. D. Crowell and D. M. Young, Trans. Faraday Soc., 49, 1081 (1953)

[6] C. Jura and D. Criddle, J. Phys. Chem. 55, 163 (1951)

2700 cal/mole at $\theta = 0.2$ to a maximum of 3400 at $\theta = 0.8$. Differential heats of adsorption have been obtained calorimetrically by Beebe and Young[7] and by Bobka *et al.*[8] for argon adsorbed on graphon. Graphon is a channel black which has been graphitized at 2700°C. There is an abundance of evidence in the literature that graphon provides an unusually uniform surface with characteristics which approximate closely those for true graphite.[1,2,9]

The graphon used by Bobka *et al.* has a surface area of 85 m^2/g and a dimension $\bar{c}$, twice the interplanar distance, of 6.96 A as compared to the value of 6.70 A for true graphite. The reported heats are in fair agreement. Bobka *et al.* give values of 2500 cal/mole at low coverages with a maximum of 3000 cal/mole at a monolayer value of about 0.85 while Beebe and Young have corresponding values of 2700 cal/mole and 3200 cal/mole. The decrease in heat of adsorption with coverage at low coverage characteristic of heterogeneous adsorbents was absent in both cases.

Neon-graphite - Pace and Siebert[10] have determined both isosteric heats from isotherms and differential heats calorimetrically

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[7] R. A. Beebe and D. M. Young, *J. Phys. Chem.* *58*, 93 (1954)

[8] R. J. Bobka, R. E. Dininny, A. R. Siebert and E. L. Pace, *J. Phys. Chem.* *61*, 1646 (1957)

[9] D. Graham, J. Phys. Chem. 61, 1310 (1957)

[10] E. L. Pace and A. R. Siebert, to be published

for neon adsorbed on the graphon sample used by Bobka *et al.* as described in the preceding section. The range of values is from 760 cal/mole at $\theta = 0.1$ to a maximum of 850 cal/mole for $\theta = 0.8$. Aston and Greyson[11] have obtained differential heats of adsorption calorimetrically for neon adsorbed on a sample of graphitized carbon specified as P-33 (2700°) by the Godfrey L. Cabot Laboratories. The $\bar{c}$ dimension was 6.80 A which is very close to the value usually ascribed to true graphite. The surface area of the sample was 12 m^2/g. The values which have been reported range from 840 cal/mole at $\theta = 0.2$ to a maximum of 950 cal/mole at $\theta = 0.8$.

Helium-graphite - Using the methods and adsorbents mentioned in the previous section, the results of Aston and Greyson[11] and of Pace and Siebert[10] are in good agreement. At low coverages ($\theta = 0.2$), the former arrive at a value of 340 cal/mole and the latter, 320 cal/mole.

Parahydrogen and orthodeuterium on graphite - Pace and Siebert[10] have determined differential heats of adsorption calorimetrically and also from isotherms around 20.4°K with graphon as an adsorbent. The values at a coverage of 0.2 monolayers is 910 cal/mole for parahydrogen and 950 cal/mole for orthodeuterium. Barrer[3] obtained values for hydrogen adsorbed on Acheson graphite which were initially 2000 cal/mole and reached a limiting value of 1100 cal/mole.

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[11] J. G. Aston and J. Greyson, *J. Phys. Chem.* *61*, 613 (1957)

Nitrogen-graphite - Pace and Siebert[10] report a calorimetric value of 2600 cal/mole at 77°K for this system. From isotherms, Barrer[3] reports an initial value of 4600 cal/mole and limiting value of 2500 cal/mole at 77°K with Acheson graphite as an adsorbent.

The data concerned with the differential or isosteric heats of adsorption of the preceding gas-solid systems are summarized in Table 1.

Since actual graphite is not the ideal surface imagined in theoretical calculations, it is necessary to resolve from the experimental data those quantities or characteristics which lend themselves to a meaningful comparison with theory. The simplest of such quantities is the one representing the interaction of a molecule of the adsorbate with the bare surface. Ideally, this should be derived from the experimental data by extrapolation to zero coverage. Because all actual surfaces are more or less heterogeneous, the experimental heat value at zero coverage does not give us the quantity we desire. On the other hand, if a value is selected for other than zero coverage, the mutual interaction of adsorbed pairs of molecules must be considered. If is fortunate that the work of investigators which has been previously mentioned has made it possible to evaluate the heterogeneity of a number of graphitized carbons. In particular, graphitized carbons such as those specified as graphon and P-33 by the Godfrey Cabot Laboratories are unusually uniform with the heterogeneity involving not more than a small percentage of the sites. Therefore, we believe that the best value for comparison

TABLE 1. Differential heats of simple gases on graphite or graphitic carbons

Gas	Adsorbent	Temp. °K	Investigator	Method	Diff. Heat cal/mole^{-1}
A	Acheson graphite	100	Barrer	isotherm	4600; 2400
	graphite (National Carbon Co.) 3.22 m^2g^{-1}; .001% ash	70-90	Jura, Criddle Everett, Young Crowell, Young	isotherm	$\theta = 0.2$; 2700 $\theta = 0.8$; 3400
	graphon (spheron, 2700°)	78	Beebe, Young	calorimetric	$\theta = 0.2$; 2700 $\theta = 0.8$; 3200
	graphon (spheron, 2700°) $\bar{c}$ = 6.96 A; 85 m^2g^{-1}	78	Bobka <u>et al.</u>	calorimetric	$\theta = 0.2$; 2500 $\theta = 0.85$; 3000
Ne	P-33, 2700° graphitic carbon; $\bar{c}$ = 6.80 A; 12 m^2g^{-1}	27	Aston, Greyson	calorimetric	$\theta = 0.2$; 840 $\theta = 0.8$; 950
	graphon (spheron, 2700°) $\bar{c}$ = 6.96 A; 85 m^2g^{-1}	27	Pace, Siebert	isotherm calorimetric	$\theta = 0.2$; 760 $\theta = 0.8$; 850
He	P-33, 2700° graphitic carbon; $\bar{c}$ = 6.80 A; 12 m^2g^{-1}	17-20	Aston, Greyson	calorimetric	$\theta = 0.2$; 340
	graphon (spheron, 2700°) $\bar{c}$ = 6.96 A; 85 m^2g^{-1}	4-20	Pace, Siebert	isotherm calorimetric	$\theta = 0.2$; 320
H_2; D_2	Acheson graphite	100	Barrer	isotherm	2000; 1100 for H_2
	graphon (spheron, 2700°) $\bar{c}$ = 6.96 A; 85 m^2g^{-1}	20-25	Pace, Siebert	isotherm calorimetric	$\theta = 0.2$; 910 for H_2 $\theta = 0.2$; 950 for D_2
N_2	Acheson graphite	100	Barrer	isotherm	4600; 2500
	graphon (spheron, 2700°) $\bar{c}$ = 6.96 A; 85 m^2g^{-1}	78	Pace, Siebert	calorimetric	$\theta = 0.2$; 2600

purposes would be obtained at coverages between $\theta = 0.1$ and $\theta = 0.2$ at which the heterogeneity of the surface is small and the effect of molecular interaction has not yet become too significant.

Using this procedure, and giving some weighting based on the reliability of the experimental procedure which has been used, the best values correct to perhaps ± 10% appear to be:
(1) 2700 cal/mole for argon-graphite system (2) 840 cal/mole for the neon-graphite system (3) 320 cal/mole for helium-graphite system (4) 910 cal/mole for the parahydrogen-graphite system
(5) 950 cal/mole for the orthodeuterium-graphite system
(6) 2600 cal/mole for nitrogen-graphite system.

II. THEORETICAL CALCULATION OF ADSORPTION ENERGIES AT ZERO COVERAGE

The Covalent Surface Model - In this model, it is assumed that no relatively long range electrostatic forces, no polarization etc. exist so that only ordinary van der Waals forces need be considered. The graphite or graphitic carbon is assumed to consist of a regular array of carbon hexagons with a spacing of 1.42 A in a layer and 3.40 A[+] between layers. The carbon atom in any one layer is over the center of the carbon hexagon in the next layer.

The interaction of an adsorbed molecule with the adsorbent is

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[+] In most of the calculations mentioned here, a spacing of 3.40 A has been assumed although more recent determination assign this value closer to 3.35 A.

approximated by the sum of the separate interactions of the adsorbed molecule with the carbon atoms in the immediate neighborhood of the adsorbed molecule. The simplest form of a potential function has an attractive and a repulsive term. The interaction per molecule-carbon atom pair can be adequately represented by a potential function of the Lennard-Jones (6-12) type,

$$u(r) = \epsilon^{*}\left[\left(\frac{r}{r}\right)^{12} - 2\left(\frac{r^{*}}{r}\right)^{6}\right] \tag{3}$$

in which the first term represents the repulsive forces and the second term the attractive forces. The preceding potential function neglects attractive terms in $1/r^{8}$ and $1/r^{10}$ which can amount to as much as 10 percent of the $1/r^{6}$ term. The total energy of interaction at a distance z above the surface is given by

$$U = \sum_{i} U(r)_{i} \tag{4}$$

obtained by summing the interactions for all carbon-molecule pairs close enough to make a significant contribution. The minimizing of the total energy with respect to z

$$\frac{\partial U}{\partial z} = 0 \tag{5}$$

establishes the equilibrium value of $z = z_{min.}$ above the surface of the graphite.

Although in principle such a procedure should give us as precise a value for the adsorption energy as we desire, in practice, uncertainties of the order of ± 10% arise because of the arbitrariness in evaluating the two parameters ϵ^{*} and r^{*} in equation (3). The sole justification for the procedure which has been used is the rather good results obtained for adsorption. For the assumed model, the attractive energy arises because of London dispersion forces involving $1/r^6$. There are a number of equations which have been used to evaluate the attractive constant $C = 2\,\epsilon(r^*)^6$ such as the London formula[12]

$$C = \frac{3}{2}\,\alpha_1\,\alpha_2\,\frac{h\nu_1\nu_2}{\nu_1+\nu_2} \qquad (6)$$

in which α_1 and α_2 are the polarizabilities of the pair of particles, h is Planck's constant, and ν_1 and ν_2 are the characteristic frequencies from the optical dispersion curve. Born and Mayer[13] suggested the replacing of the constant 3/4 by 9/4 in order to better reproduce particle interaction. Also, ionization potentials I_1 and I_2 may be used to replace $h\nu_1$ and $h\nu_2$ in equation (6). The preceding equations in practice tend to give too low values for the dispersion energy. Therefore, following the procedure used with considerable success by Barrer and by Orr[14] in adsorption studies, the present work makes use of the Kirkwood-Müller formula[15] for the attractive constant.

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[12] F. London, Z. Phys. Chem. B 11, 221 (1930)

[13] M. Born and J. E. Mayer, Z. Phys. 75, 1 (1952)

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

[14] A. Müller, Proc. Roy. Soc. (London) A154, 624 (1936)

$$C = 6mc^2 \frac{\alpha_1 \alpha_2}{\frac{\alpha_1}{\chi_1} + \frac{\alpha_2}{\chi_2}} \tag{7}$$

in which m is the mass of the electron; c, the velocity of light; α_1 and α_2, the polarizabilities; and χ_1 and χ_2, the diamagnetic succeptibilities of the pair of particles.

The method of choosing a value r^*, the equilibrium spacing of the carbon-molecule pair, is the most controversial point in the entire procedure among investigators. The controversy emphasizes the lack of knowledge of the repulsive forces active in adsorption. Barrer[3] described the r^* used in his calculations on the equilibrium distance from the solid (= 3.7 A) and therefore a distance a little greater than the mean of the interlaminar distance in graphite and the internuclear distances for hydrogen, argon and nitrogen used as absorbates. Crowell and Young[5] maintained that the method of Barrer had no meaning and selected an $r^* = 4.05$ A such that the calculated equilibrium distance above a carbon atom in the basal plane was equal to 3.60 A, which is half the sum of the interlaminar distance in graphite and the equilibrium spacing of two argon atoms (3.85 A) for the case of argon adsorbed on graphite. It appears to us that Barrer's[3] description of r^* is incorrect but that his use of it is more correct than Crowell and Young's[5]. The only description we can see for r^* is the equilibrium separation at the potential energy minimum for the adsorbed molecule-graphitic carbon pair. We have adopted the criterion of Barrer[3] and have taken r^* to be the mean of the spacing of graphite layers and the equilibrium spacing of a pair of molecules of the adsorbate from second virial coefficient or viscosity data.

Investigators have used a variety of methods in obtaining the total energy of adsorption by summing the interactions of individual molecule-carbon atom pairs as the molecule approaches the adsorbent surface. Hill[16] assumes the surface to be a continuum and replaces the summation with an integration. The resulting expression is

$$U = \frac{\epsilon r^{*12} \pi \rho}{45 z^9} - \frac{\epsilon r^{*6} \pi \rho}{3 z^3} \qquad (8)$$

in which ρ is the density of carbon atoms in the unit of number carbon atoms per cc. The equilibrium position above the surface is given by

$$z_{min.} = 0.765\ r^* \qquad (9)$$

and the energy at minimum by

$$U_o = \frac{2\sqrt{5}}{9} \epsilon r^{*3} \pi \rho \qquad (10)$$

Crowell[17] uses a procedure which integrates the contributions layerwise, assuming that each layer has the atomic density of graphite and that the spacing of the layers corresponds to that for graphite.

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[16] T. L. Hill, Advances in Catalysis, Vol. IV, Academic Press Inc., New York, New York, 1952, p. 214

[17] A. D. Crowell, *J. Chem. Phys.* **26**, 1407 (1957)

For the case of argon adsorbed on graphite, the procedure of Hill[16] yields approximately one-half and that of Crowell[17] about two-thirds of the observed value of approximately 2700 cal/mole. This is not surprising in that the procedures essentially assume a completely random distribution of carbon atoms and thus neglect the most important contribution from the nearest group of atoms in an ordered structure.

Barrer[3] used a summation procedure in which the contributions of the nearest 100 atoms were added. Pace[18] carried out a summation for all carbon atoms within 6 A of the adsorbed molecule in order to account for the important contribution of the closest atoms and integrated over the remainder for the case of argon adsorbed on graphon. For a number of low boiling gases adsorbed on graphon, Pace and Siebert[10] have carried out a summation over all atoms within a 10 A range and an integration for carbon atoms beyond this distance. Crowell and Young[5], in repeating Barrer's calculation of argon adsorbed on graphite, used a summation procedure entirely.

The calculated value cannot be compared directly with the observed value at low coverage because (1) the experimental heats are observed at temperatures other than absolute zero (2) a change in the nature of the degrees of freedom occurs when the molecule is adsorbed.

The calculated value of energy U can be identified with

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[18] E. L. Pace, *J. Chem. Phys*. *27*, 1341 (1957)

either the differential energy or differential heat of adsorption at absolute zero. A temperature correction must be applied

$$\int_0^T (C_{pg} - \bar{C}_{N_s})\, dT \tag{11}$$

in which C_{pg} = heat capacity of the gas at constant pressure

$\bar{C}_{N_s}$ = partial molar heat capacity of the adsorbed gas.

Since the curve of $\bar{C}_{N_s}$ vs T crosses that of C_{pg} vs T, to a certain extent the amount of the contribution of this quantity is cancelled. In any case, in the absence of specific information on the heat capacity of the adsorbed phase, the contribution is neglected.

The three translational degrees of freedom for a monatomic molecule become one vibrational degree of freedom for the motion perpendicular to the surface and two degrees of freedom for the motion in the plane of the surface. For a polyatomic molecule, additional rotational degrees of freedom are also involved. The degrees of freedom involving the plane of the surface may be more or less restricted depending on the energy barriers to the particular motion arising from neighboring adsorbent or adsorbate atoms. For most of the systems studied, the temperatures are such that the barriers to translational and rotational motion on the surface are not critical and the neglect of this effect will introduce an uncertainty of the order of RT calories per mole.

In Table 2, the results of the theoretical calculation of

TABLE 2. Comparison of calculated and observed heats of adsorption

Gas	r^* A	z A°	Investigator	Zero Point Energy cal/mole	Calculated Energy, U^a cal/mole^{-1}	Observed Diff. Heat Best Value, cal/mole^{-1}
Argon	3.7	——	Barrer		2520	2700
	4.05	3.60	Crowell, Young		1750	
	——	3.59(?)	Crowell		1800	
	3.61	3.18	Pace		2470	
	3.62	3.18	Pace, Siebert	80	2780	
Neon	3.24	2.86	" "	60	950	840
Helium	3.16	2.80	" "	90	330	320
Hydrogen	3.34	2.95	" "	200	880	950
Deuterium	3.34	2.95	" "	140	820	910
Nitrogen	3.75	3.30	" "	90	2180	2600

[a] At center of surface hexagon

the energy of interaction of various simple gases with graphite are compared with the differential heat at low coverage which has been deduced from a number of experiments with graphite and graphitic surfaces. Uncertainties of the order of ± 10% probably exist because of approximations in the theoretical method, ignorance of the surface and uncertainties of procedure in the experimental method.

III. THE ZERO POINT ENERGIES

The zero point energy for the molecule vibrating in the potential well for motion perpendicular to the surface can be roughly approximated from the curvature at the minimum.

If z is the distance above the surface and z_o the distance above the surface at the potential energy minimum, a power series expansion of the energy around z_o is

$$U = f(z_o) + f'(z_o)(z - z_o) + f''(z_o)(z - z_o)^2/2! + \ldots\ldots \qquad (12)$$

in which $f(z_o) = U_o$ and $f'(z_o) = 0$.

By neglecting higher powered terms, we arrive at the usual expression for a harmonic displacement with a frequency in this case equal to the zero point frequency ν_o.

$$\nu_o = (1/2\pi)\left[f''(z_o)/m\right]^{1/2} \qquad (13)$$

For the case of a continuous solid the method of Hill[16] gives

$$\nu_o = 2.583 \quad (\epsilon^* \; r^* \rho/m\pi)^{1/2} \qquad (14)$$

and results in frequencies of the right order of magnitude, 10^{12} sec^{-1}.

For the case of a graphite surface of discrete particles, the zero point frequency can be evaluated by a summation procedure after performing the necessary differentiations on U_o to give

$$f''(z_o) = \sum \epsilon^* \left(\frac{156\ r^{*12}}{r^{14}} - \frac{84\ r^{*6}}{r^8} \right) \tag{15}$$

with the r's evaluated with the molecule at z_o. Pace and Siebert[10] used this procedure for the case of various simple gases adsorbed on graphite in a position over the center of a carbon hexagon. Summation over the nearest 54 carbon atoms was significant. The zero point energy was then related to the frequency by the expression

$$\epsilon_o = \frac{1}{2}\ h\nu_o \tag{16}$$

The results are presented in Table 2. For the case of the higher boiling gases such as nitrogen and argon, the zero point energy is of the order of 100 calories and is less than 5% of the total heat. In the case of the lowest boiling gases, helium, parahydrogen and orthodeuterium, it is a sizeable fraction of the adsorption energy. In particular, it is of interest to note that in the case of parahydrogen and orthodeuterium, it accounts satisfactorily in order of magnitude for the difference in the differential heats of adsorption which have been observed at low coverage.

IV. THE ROLE OF BARRIERS ON THE SURFACE OF GRAPHITE

For an assumed ideal graphite surface and interaction forces described by a Lennard-Jones (6-12) potential, it is possible to use the procedure introduced by Barrer[3] for argon on graphite and expanded in great detail by Orr[14] for the case of argon adsorbed by alkali halide, to determine the nature of barriers in the surface. This is accomplished by minimizing the interaction contributions from surface atoms with respect to distance z above the surface for approaches normal to various points on the surface itself. In Table 3, the value of this energy for approaches (1) above the center of surface hexagon (2) over an apex carbon and (3) at the midpoint between two carbon atoms on the surface which has been calculated by various investigators is shown. Although there is general disagreement on the absolute magnitude of the calculated energies of the sites, there is agreement on the order of the difference between the energies for the sites. Therefore, it appears reasonable to assume that a periodic barrier of the order of 200 calories per mole (approximately RT calories) exists in three directions as one passes between hexagon centers either over the midpoint of the side or the apex of a carbon hexagon. Important conclusions follow. First, the movement of adsorbed argon molecules is mobile over the surface. With the interaction of two argon atoms at the equilibrium distance evolving 238 calories per mole (ϵ^*), it is obvious that as the coverage of the surface increases the effect of surface barriers will become increasingly unimportant, and some type of "packing" of the molecules will be favored.

V. HEAT OF ADSORPTION FROM LATTICE LIQUID THEORY

The presence of small energy barriers (<RT per mole) discussed in the preceding section suggests a model for adsorption which

TABLE 3. Surface energy barriers for argon adsorbed on graphite.

Position	Site	Adsorption energy U_o, cal mole^{-1}		
		Barrer*	Crowell, Young	Pace
Above center of hexagon	a	2520	1750	2470
Above carbon atom	b	2130	1710	2360
Midpoint between two carbons	c	2210	1710	2380

* No correction was made for zero point energy.

might be used to explain both monolayer and multilayer adsorption. The molecules are anchored quite strongly in a direction perpendicular to the surface but are essentially unrestricted in their motion in the plane of the surface. This is exactly the situation which would favor some type of packing, e.g. hexagonal packing, as the number of molecules on the surface increases. It also would mean that adsorption would tend to take place in layers, with the layers showing some of the behavior associated with liquids or dense gases. The model described in the general manner above has been used[18] to characterize the differential heat of the adsorption which has been observed experimentally by Beebe and Young[7] for argon adsorbed on graphon (spheron, 2700°) for coverage to about two monolayers.

The general characteristics observed in the experimental heat of adsorption are: (1) a maximum at $\theta = 0.8$ to 0.9 at which the heat value is approximately 3200 calories per mole (2) a minimum value of the order of the heat of liquefaction (1700 cal/mole) at θ slightly greater than one and (3) a second maximum at $\theta = 2$ with a heat value of 2000 cal/mole.

Any liquid theory treatment is difficult if an exact treatment is desired. In the usual treatment, so many approximations are introduced as to render doubtful the value of the results.

On the other hand, lattice liquid theory has been used with fair success in treating the properties of dense gases such as critical pressure, density, etc. of bulk gases. A critical discussion of lattice liquid theories applied to ordinary liquids has been given by Rowlinson and Curtiss[19].

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[19] J. A. Rowlinson and C. F. Curtiss, J. Chem. Phys. 19, 1519 (1951)

When application of lattice liquid theory is considered here, some of the features are appealing, such as (1) the idea of limited motion within a cell composed of nearest neighbors (2) the interaction with a number of geometrically arranged neighbors (3) the relative simplicity of the treatment which makes it possible to arrive at numerical values for comparison with observed values.

The application of the theory in detail depends on the choice of (a) the size of the cell, i.e., the area for movement of a single molecule and (b) the parameters involving the variation of the cell size with fraction of vacant sites or holes in the lattice.

The BET theory has enjoyed considerable success in determining surface area based on cross-sectional molecular areas derived from an assumed hexagonal close-packed liquid phase for the monolayer. Consequently, it appears reasonable to make this fact the basis of the selection of a cell size for our model. Therefore, let us divide the surface area of the solid into a number of cells such that, at the monolayer capacity, there will be one molecule for each cell. If the molecules are in a hexagonal close-packed layer with the density of the bulk liquid, the apportioning of the surface area in the manner specified above will give a cell area of $(\sqrt{3}/2)a^2$ where a is the equilibrium spacing between nearest neighbors. At the limit of zero coverage, the free area available for motion of the molecule about the center of a cell has a maximum value equal to cell area. It is possible, in general, to integrate the following expression for the free area available to a molecule:

$$j_{\omega} = a^2 \int_0^{\sqrt{3}/(2\pi)} \exp\left\{(1-\omega)(c/\tau) \times \left[2\,q^{-3}\,m(y) - q^{-6}\,\ell(y)\right]\right\} dy \qquad (17)$$

in which

ω = fraction of vacant sites around a lattice site

$y = r^2/a^2$; r, the separation of two molecules and a, the equilibrium spacing of two molecules

c = coordination number of lattice, i.e., 6 for hexagonal packing

q = reduced cell size $(\sqrt{3}/2)a^2/(\sqrt{3}/2)r^{2}$

τ = reduced temperature = kT/ϵ^*

ϵ^*, r^* = parameters in the Lennard-Jones (6-12) potential

$m(y) = (1 + dy + y^2)(1 - y)^{-5} - 1$

$\ell(y) = (1 + y)(1 + 24y + 76y^2 + 24y^3 + y^4)(1 - y)^{-11} - 1$

In establishing a partition function from which thermodynamic properties can be obtained, it is necessary to consider the variation of the free area j_{ω} with the fraction of vacant sites in the lattice ω. The simplest of such expressions approximating this variation, the so-called Ono approximation[19], has been used in obtaining the expressions which follow. Actually, the approximation is correct only at the limits of zero and monolayer coverage.

Another approximation which has been introduced is that each of the molecules adsorbed in a surface layer provides an adsorption site for a succeding layer. This is most true for high coverages for a layer and neglects "edge" effects.

Finally, it is assumed that the distribution of molecules adsorbed in any layer is completely random. If each occupied site has a neighbors, a perfectly random arrangement gives a probability of N_i/N_{i-1} for occupation for the case of N molecules adsorbed on N_{i-1} sites on the layer below it. Hence, the average number for any given N_i is cN_i/N_{i-1} and total number of neighboring pairs for N_i molecules is $(cN_i/N_{i-1}) \times N_i \times 1/2$, the 1/2 being introduced to avoid double counting.

The partition function Q for an assembly of N molecules, N_i in each layer, adsorbed in i layers including the above approximations is

$$Q = \prod_i \left\{ \exp\left(-N_i \chi_i/kT\right) \right\} \left\{ (2\pi mkT j_1/h^2)^{N_i} \right\}$$

$$\times \left\{ \frac{N_{i-1}!}{(N_{i-1} - N_i)!\, N_i!} \exp\left[(N_i^2/N_{i-1})(c\psi_i/2kT) \right] \right\} \qquad (18)$$

in which

$$\psi_i = -\left[u_i - (2kT/c \ln(j_1/j_0) \right] \qquad (19)$$

and

$$u_i = \epsilon^* \left[(r^*/r)^{12} - 2(r^*/r)^6 \right] \qquad (20)$$

with the restriction that

$$N = \sum N_i \qquad (21)$$

The two equations above properly maximized with respect to the N_i's (with the total number of molecules constant) leads to the equilibrium population of the sites. The integral energy of adsorption is given by

$$E = kT^2 \ (\partial \ln Q/\partial T)_{N,N_0} \qquad (21)$$

and the isosteric heat by

$$q_{st} = -(R/k) \ (\partial E/\partial N)_{T,N_0} + RT \qquad (22)$$

A calculation has been carried out assuming that the adsorption involves three layers. Site energies are determined in the following manner. In the first layer, the procedure previously mentioned for the case of an isolated molecule on a graphite surface is used. The results are summarized in Table 3. Rather than deal with the small energy barriers in the surface, the surface is assumed homogeneous by an averaging procedure weighting the sites a, b, c in Table 3 by the ratio of 1:3:2. In the second layer, a molecule is assumed to position itself on a triangle of molecules in the first layer which is hexagonally close-packed with the usual liquid parameters. Appropriate integration or summation procedures for the interaction of the approaching molecule with the adsorbed molecules in the first layer and the carbon atoms in the graphite surface are used. The molecules in the first layer are assumed to remain fixed while the approaching molecule in the second layer attains its equilibrium position. This procedure is followed essentially in obtaining the energy for the third layer sites.

The final results of the calculation are given in Table 4 and compared with the observed curve of adsorption heat versus coverage in Fig. 1. The agreement is better than one should have

TABLE 4. The calculated differential energy of adsorption of argon on graphon.

$\chi_1/kT = -13.69$ $\quad$ $\chi_2/kT = -7.42$ $\quad$ $\chi_3/kT = -6.13$

$g = 0.01329$ $\quad$ $g_A = -0.00918$ $\quad$ $T = 87.5°K$

θ	$q_{st.}$ cal/mole
0.50	3085
0.60	3191
0.70	3298
0.81	3386
0.91	3415
0.96	3102
1.01	2379
1.04	1834
1.10	1639
1.21	1662
1.44	1804
1.70	1898
1.85	1917
2.03	1881
2.15	1867
2.31	1878

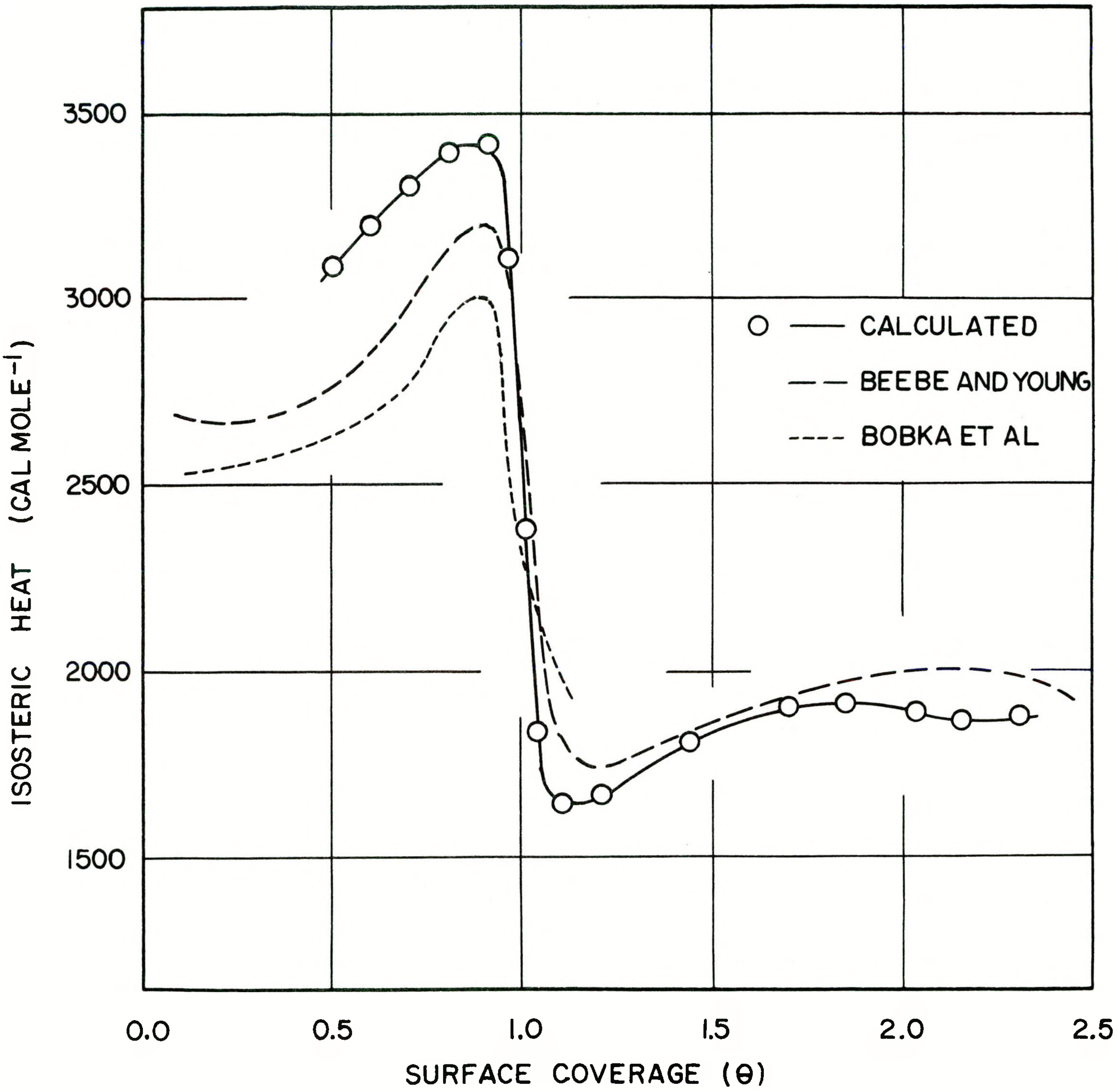

Fig. 1. Comparison of calculated and observed isosteric heat of adsorption for argon-graphon at 87.5°K.

reason to expect from the nature of the approximations which have been introduced in the development of the model. The model, however, would be expected to fail at high coverages because the adsorption has been assumbed to involve a limited number of layers.