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ADSORPTION OF RARE GASES ON A RARE GAS SURFACE+

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Experimental adsorption heats and isotherms for He, Ne and Ar adsorbed on a xenon-covered sample of carbon black are analyzed to obtain several thermodynamic properties which characterize the behavior of isolated adsorbed atoms and pairs of atoms on the surfaces. The experimental results are compared with theoretical estimates of these quantities which are obtained by evaluating the appropriate statistical mechanical expressions with the aid of the computed potential energy functions for the gas atoms interacting with the solid and with each other. Reasons for the discrepancies between theory and experiment are discussed, and some conclusions are drawn concerning the surface distribution of the adsorbed atoms in these systems.

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INTRODUCTION

Studies of the adsorption of rare gases on surfaces which have been prepared by preadsorbing a layer of another higher boiling rare gas on a high area substrate can provide valuable data for comparison with theoretical calculations of the thermodynamic properties of adsorbed atoms. Since the parameters of the intermolecular potential energy functions for pairs of rare gas atoms are relatively well known, one can make reasonably accurate estimates of the energy of interaction of a gas atom with the solidified rare gas layer plus the original substrate by summing the pair-wise energies of the gas atom with the atoms of the adsorbent. With the aid of these potential surfaces, one can then compute energies of adsorption in the limit of zero coverage, free energies of isolated adsorbed atoms, and the most probable positions of the adsorbed atoms relative to the lattice structure of the surface. Although such calculations are feasible only if it is assumed that the surface of the solid is present as a perfect crystalline array, experimental systems which approximate this model can be obtained if the substrate is carefully chosen and if the preadsorbed gas is carefully laid down on the substrate and cooled to the experimental temperatures, which are preferably well below the freezing point of the preadsorbed substance. In this paper, experimental data are presented for several gases adsorbed on a monolayer of xenon which had been preadsorbed on a graphitized carbon black with a specific area of 70 m^2/g. The results of some previous work on the properties of argon adsorbed on such surfaces at 65 - 80° K. are included for completeness (1,2); however, measurements of the isotherms and heats of adsorption for neon from 20 - 24° K. and helium from 11 - 13° K. are also reported, and the thermodynamic properties obtained from the low coverage portion of the data are compared with theoretical predictions. In the theoretical work, two possibilities for the lattice structure of the preadsorbed xenon layer are considered: that of a triangular, and that of a square array. Although the previous analysis of the argon adsorption data had led to the tentative conclusion that the xenon was square packed, the more extensive data reported here do not lend further weight to this deduction. (In fact, recent LEED measurements indicate that xenon monlayers on graphite surfaces have triangular packing at low temperatures. (3)).

EXPERIMENTAL

The apparatus used in this work has been described in detail elsewhere (4). It consists of a simple calorimeter in which the adsorbent-filled container is surrounded by an electrically heated shield which is suspended in an evacuated can. With the can immersed in liquid or solid hydrogen, the temperature of the sample could be set and held constant to within 0.001°K. at any temperature from 11° to 25° K. The thermometer used in this range was a carbon radio resistor which had been calibrated against a platinum resistance thermometer of lower sensitivity and checked at the boiling point and the triple point temperatures of hydrogen. Isotherms were determined for neon at 20.39° and 23.17°K., and for helium at 11.57° and 12.54°K. which included coverages ranging up to roughly one monolayer. In addition, heats of adsorption were determined calorimetrically for neon in order to check the heats obtained from the temperature dependence of the isotherm data. Plots of the heats of adsorption as a function of the coverage are shown in Figure 1 for helium, neon and argon on the xenon-covered carbon black. As expected, both the heat at zero coverage and the change in the heat with increasing coverage increase substantially as one progresses from helium to argon. The curves shown in this figure were used together with the low coverage portions of the isotherms to calculate several properties of theoretical interest. The determination of these parameters is based on earlier work in which it was shown that (5):

$$\lim_{\theta=0} (\theta/p) = Z_s/kT + \theta\beta_2 (Z_s/kT) \qquad (1)$$

and

$$\lim_{\theta=0} q_{st} - RT = -L(\epsilon_1 + \theta\epsilon_2) \qquad (2)$$

where θ is the fraction of surface sites covered, Z_s is the configurational integral for a single adsorbed atom on one of the surface sites, and ϵ_1 is classically the average potential energy of an isolated adsorbed atom; L is Avagadro's number; β_2 is the second virial coefficient for

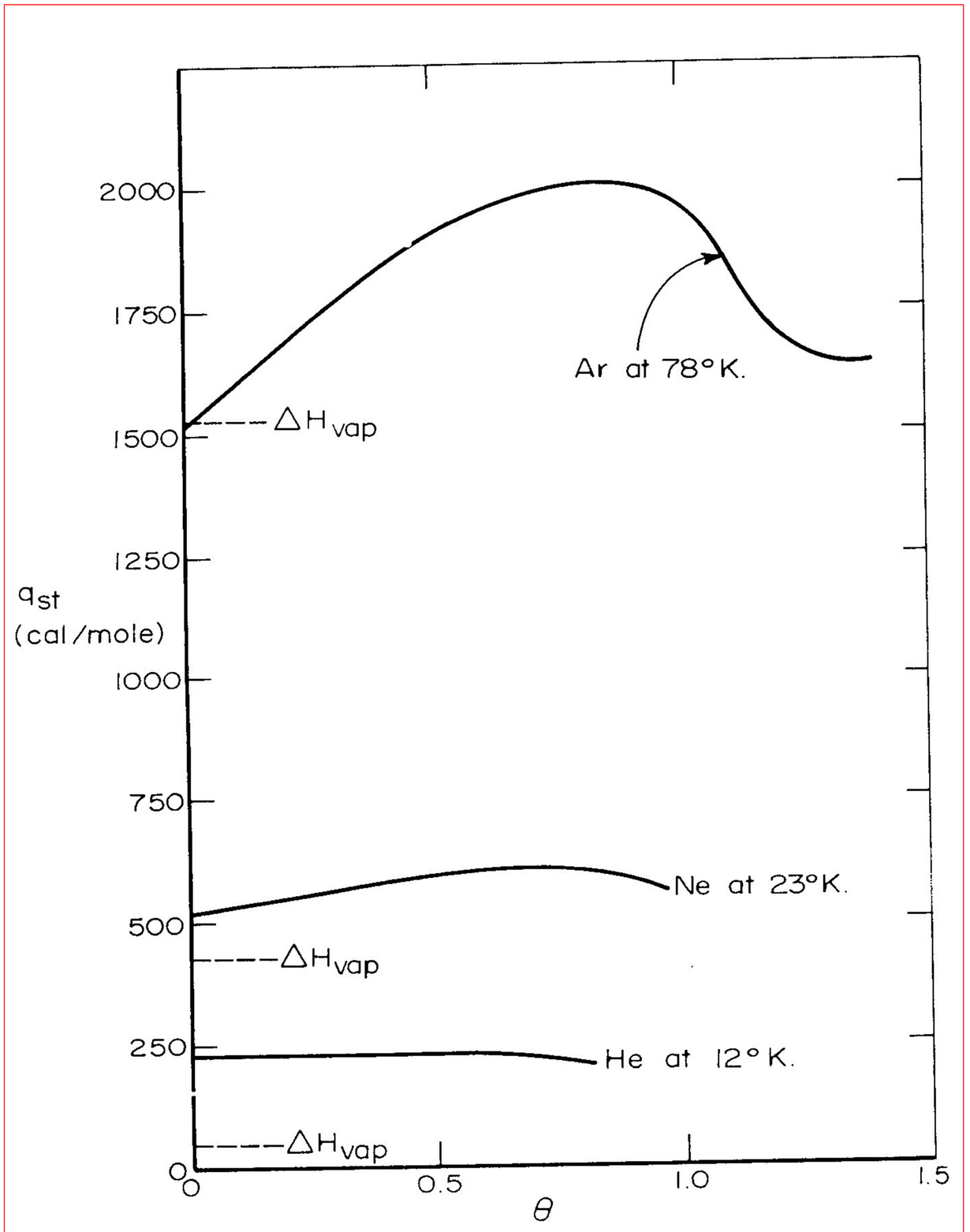

Figure 1. Heats of adsorption as a function of the surface coverage for rare gases on a xenon-covered surface.

a pair of adsorbed atoms and ϵ_2 is the average lateral interaction energy of an isolated pair of adsorbed atoms. It is evident that such quantities can readily be compared with theoretical values based on the estimated potential energies of the adsorbed atoms with the surface and with each other when the appropriate quantum expressions for Z_s, ϵ_1, and the pair parameters are introduced. The experimental values of these parameters which are reported in Table 1 were calculated by fitting the data obtained in this work for He and Ne to Eqs. (1) and (2). In addition, some data were obtained for Ar in this work which checked earlier results (1), but which were concentrated in the low coverage region and thus gave more reliable values for the parameters shown for this substance in Table 1. The estimated uncertainties in the tabulated quantities are 3% for Z_s and ϵ_1 and 20% for β_2. The values of ϵ_2/k are probably accurate to 10^o for He and Ne and 25^o for Ar.

Table 1. Experimental Values of the Properties of Atoms adsorbed on a Xenon-Covered Substrate.

	Z_s (a) (Å.^{3}/site)	Z_s/A_s (Å.^{3}/Å.^{2})	β_2	ϵ_1/k (deg.K.)	ϵ_2/k (deg. K.)
He at 12.5° K.	$8.0 \cdot 10^3$	$4.3 \cdot 10^2$	-1.2	-100	0
Ne at 23.2° K.	$16.7 \cdot 10^3$	$9.0 \cdot 10^2$	0.9	-240	-52
Ar at 79.2° K.	$53.9 \cdot 10^3$	$29.0 \cdot 10^2$	1.5	-700	-260

(a) Calculated assuming that the site area $A_s = 18.6$ Å.^{2}.

THEORETICAL

Potential energy surfaces were constructed for isolated He, Ne and Ar atoms over simple square and triangular xenon monolayer lattices adsorbed on a graphite basal plane. The energy of the adsorbed atom Y was obtained by summing the pair-wise Y-Xe energies over the Xe layer and adding a term to this sum which accounts of the interaction of Y with the graphite substrate:

$$u_s(r) = 4\,\epsilon_{Y\text{-}Xe} \sum_i \left\{ \left(\frac{\sigma_{Y\text{-}Xe}}{r_i} \right)^{12} - \left(\frac{\sigma_{Y\text{-}Xe}}{r_i} \right)^{6} \right\} - \epsilon_{Y\text{-}C}\, \psi^{(3)}(z'_{Y\text{-}Xe}/d) \qquad (3)$$

where $\epsilon_{Y\text{-}Xe}$, $\epsilon_{Y\text{-}C}$ are the parameters which characterize the strengths of the interaction of a Y atom with a Xe atom and with the atoms of carbon in the graphite, respectively; $\sigma_{Y\text{-}Xe}$ is the distance scaling parameter in the Leonard-Jones expression for the Y-Xe potential function, $z'_{Y\text{-}C}$ is the distance between the atom of Y and the surface of the graphite and d is the separation distance between successive basal planes in the graphite crystal; and $\psi^{(3)}$ denotes the generalized zeta function of order three. Values of $\epsilon_{Y\text{-}C}$ were calculated from the equations given by Crowell and Steele (6) and are listed in Table 2 together with the values of $\epsilon_{Y\text{-}Xe}$ and $\sigma_{Y\text{-}Xe}$ which were obtained from the geometric mean (for ϵ) and the arithmetic mean (for σ) of the tabulated parameters for the Y-Y and the Xe-Xe Lennard-Jones potential curves (7). The Xe-Xe spacing in

Table 2. Parameters of the Gas-Solid Potential Functions

Y	$\epsilon_{Y\text{-}C}/k$ (deg. K.)	$\epsilon_{Y\text{-}Xe}/k$ (deg. K.)	$\sigma_{Y\text{-}Xe}$ (A.)
He	20°	47°	3.30
Ne	88°	88°	3.40
Ar	297°	166°	3.74

the surface layer (which is denoted by a in this paper) was assumed to be equal to that in the bulk crystal at 0° K., and was thus taken to be 4.31 Å. In this way, the summation over all values of r_i, the distance between the Y atom and the i'th atom in the xenon layer, could be carried out by a computer and the energy defined in Eq. 3 could be obtained for a number of positions of the Y atom relative to the Xe lattices. The perpendicular distance of Y above the surface was varied until the position, depth and curvative of the energy curve at its minimum was found for each position. The values of these minima are shown in Figure 2 as a function of the x-coordinate of the adsorbed atoms. The origin of the coordinate axes was taken to be at the center of a square or a triangle of xenon atoms and the x direction was defined to lie along the bisectors of the square and triangle. Thus, $x/a = {}^1/_2$, $y/a = 0$ corresponds to a Y atom above the midpoint of a line connecting a pair of Xe atoms in the square lattice, and $x/a={}^1/_2$, $y/a={}^1/_2$ corresponds to the atom directly above a Xe atom, whereas x/a=.288, y/a=0 corresponds to

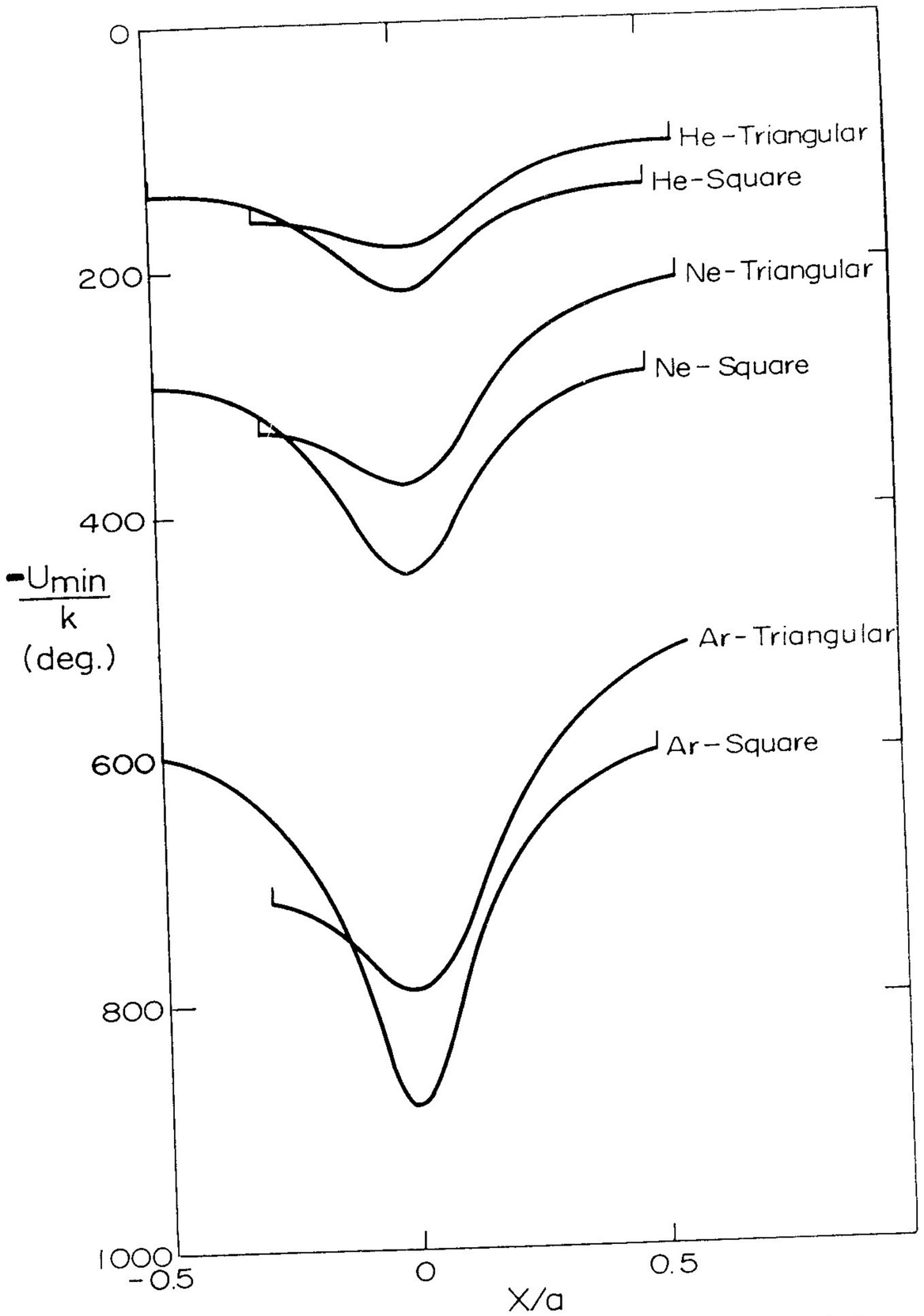

Figure 2. Variation in the computed minimum potential energies with displacements parallel to the surface for rare gas atoms over a xenon covered surface.

the Y atom above the mid-point of a line connecting a pair of Xe atoms in the triangular lattice, and x/a=.576, y/a= 0 corresponds to the position directly over the Xe atom. It is evident that the differences between the energies at the end point of the curves in Figure 2 and the values at the points with x/a=0 correspond to the heights of the barriers to translation across the surface. Since these barriers are greater than kT at the experimental temperatures for the gases considered, the adsorption is best described as sitewise rather than as a two-dimensional gas. The square-packed xenon lattice is now seen to consist of an array of square adsorption sites with areas of 18.6 Å.^{2} each, and the triangular array consists of triangular sites of areas equal to 8.1 Å.^{2} In either case, the sites are defined by the xenon atoms which are present at each corner.

The fact that the adsorbed atoms will most probably be located at or near to the center of the sites formed by the array of xenon atoms will greatly affect the interaction energies of pairs of neighboring adsorbed atoms. In the case of the square xenon lattice, one Y atom will be adsorbed per square xenon site and the Y-Y distances, which are determined by the Xe-Xe spacings, will be 4.31 Å., $\sqrt{2}\cdot$4.31 Å., etc. On the triangular lattice, the situation will be more complex, since the Y atoms are in general too large to be accommodated on nearest neighbor pairs of sites. Figure 3 shows schematically a possible arrangement of a "complete" adsorbed layer of atoms on triangular sites; the circles indicate the σ_{Y-Y} values, which are roughly equal to the hard sphere radii of the adsorbed atoms and the dotted lines are drawn through the xenon lattice points and thus outline the site boundaries. It is evident that only half the sites can be occupied when a complete layer of Ne or Ar is adsorbed; although the sketch for adsorbed helium would seem to indicate that these atoms are small enough to be accommodated on nearest neighbor sites, it is probable that the amplitude of the zero point vibrations of the helium atoms is large enough to prevent the occupancy of nearest neighbor sites, at least until all the more energetically favorable sites are occupied.

It is now possible to use these computed potential functions to calculate values for the thermodynamic properties of the adsorbed atoms which can be compared with the experimental results tabulated in Table 1. If one

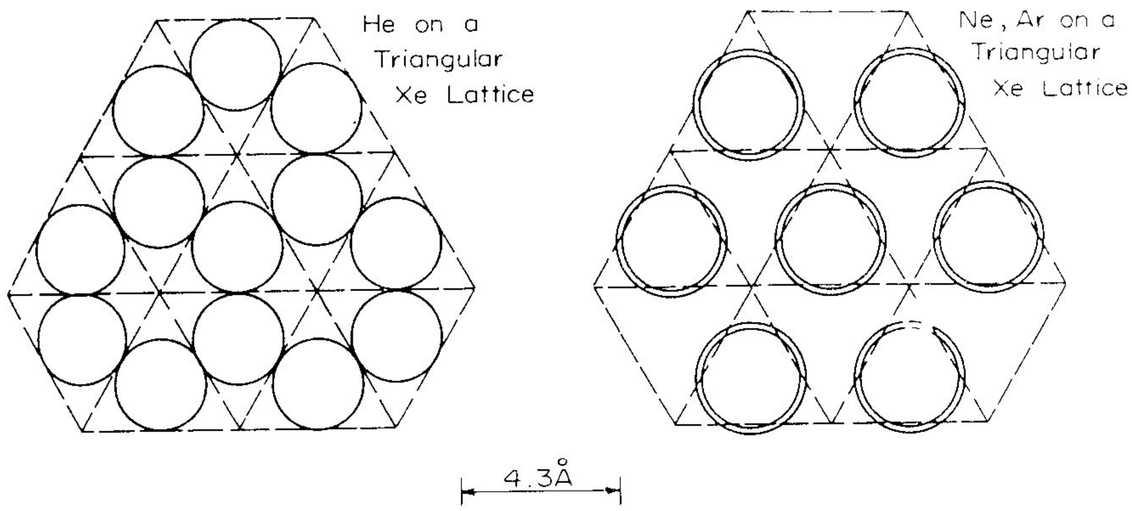

Figure 3. Possible packings of atoms on sites for a triangular xenon lattice.

starts by considering the properties of the isolated atoms, one can write:

$$Z_s = v_f^{(s)} \, e^{-(\epsilon_{min} + \epsilon^o)/kT} \qquad (4)$$

$$\epsilon_1 = \epsilon_{min} + \epsilon^o + \langle\epsilon_{th}\rangle \qquad (5)$$

where ϵ_{min} is the minimum potential energy of an adsorbed atom, ϵ^o is the total zero point vibrational energy and $\langle\epsilon_{th}\rangle$ is the change in the average potential energy due to thermal excitation; $v_f^{(s)}$ is the free volume occupied by an atom adsorbed on a site. Inasmuch as the adsorbed helium is far from behaving classically, both the quantum mechanical and the limiting classical expressions for $v_f^{(s)}$ and $\langle\epsilon_{th}\rangle$ will be required. Quantum mechanically,

$$v_f^{(s)} = \Lambda^3 \sum_j e^{-[\epsilon(j)-(\epsilon_{min}+\epsilon^o)]/kT} \qquad (6)$$

$$\langle\epsilon_{th}\rangle = \sum_j \epsilon(j) \, P(j) - 3/2 \, kT \qquad (7)$$

where $\Lambda = (h^2/2\pi mkT)^{1/2}$, $\epsilon(j)$ is the j'th energy state of the atom in the potential well at the surface of the solid; P(j) is the probability that the atom will be in

the j'th state, and is given by a simple normalized Boltzmann factor. The term of 3/2 kT in Eq.(7) is included to correct for the fact that the first term on the right gives the total thermal energy, whereas one actually wants the effective average potential energy in the quantum case. The classical limits of Eqs. (6) and (7) are:

$$v_f^{(s)} = \int_{V_s} e^{-[\epsilon(\underset{\sim}{r})-(\epsilon_{min} + \epsilon^o)]/kT} d\underset{\sim}{r} \qquad (8)$$

$$\langle\epsilon_{th}\rangle = 1/v_f^{(s)} \int_{V_s} [\epsilon(\underset{\sim}{r})-(\epsilon_{min} + \epsilon^o)] e^{-[\epsilon(\underset{\sim}{r})-(\epsilon_{min}+\epsilon^o)]/kT} d\underset{\sim}{r} \qquad (9)$$

where V_s denotes the volume over a site in which the gas-solid interaction is appreciable compared to kT.

In the previous work on adsorbed argon (2), it was shown that the classical limiting equations apply rather well. Theoretical values of the free volume and the average potential energy were evaluated by substituting the computed potential surface for argon atoms over the square and triangular xenon sites into Eqs. (8) and (9) and performing the indicated integrations. After a small quantum correction was also computed, results were obtained for the various terms in Eq. (5) for the energy of an isolated adsorbed argon atom which are shown in Table 3. In addition, the calculated free volumes and configurational integrals are shown in Table 4. In order to compute a value for Z_s, it is of course necessary to estimate the minimum potential energy of the adsorbed argon atoms; inasmuch as these calculations are very sensitive to the choice of this energy, the best experimental estimate of the energy was taken rather than the theoretical energies which are sufficiently inaccurate to give totally unrealistic results for Z_s. The energies used in this calculation were obtained by substituting the experimental values of ϵ_1 and the theoretical values of $\langle\epsilon_{th}\rangle$ for He and Ne, and $\langle\epsilon_{th}\rangle + \epsilon^o$ for argon in Eq. (5). The numerical values which resulted are indicated in Table 4. The calculated parameters for isolated adsorbed He and Ne atoms are also given in Tables 3 and 4. These computations required a knowledge of the energy levels of the atoms. Although it was possible to solve the wave equation for a simplified representation of the potential function for the atoms over a square site, the problem has not yet been

solved for the triangular lattice, except for the ground state. In this case, the potential variation can be approximated by a purely radial harmonic oscillator function for displacements parallel to the surface plus a perturbed harmonic function for displacements perpendicular to the surface (for small displacements). In the case of helium, it appears that only the ground vibrational state is populated even at 13°K., so that the detailed spacing of the higher levels is not needed in the calculation of the thermodynamic properties. For neon on a triangular site, the thermal energies and free volumes have been assumed to be roughly equal to those for the square site; The parameters estimated in this fashion are distinguished from those which have actually been calculated in Tables 3 and 4 by being enclosed in parentheses. It is evident that

Table 3. Theoretical Values for the Energies of Isolated Atoms Adsorbed on Xenon Lattices (Units in deg. K.)

	Square				Triangular			
	ϵ_{min}/k	ϵ^o/k	$\langle\epsilon_{th}\rangle/k$	ϵ_1/k	ϵ_{min}/k	ϵ^o/k	$\langle\epsilon\rangle_{th}/k$	ϵ_1/k
He, 12.5°	-220	90	-20	-150	-185	80	-20	-125
Ne, 23.2°	-450	60	-10	-380	-375	50	(-10)	-335
Ar, 79.2°	-885	60	150	-675	-790	50	-95	-645

theoretical estimates for ϵ_1 and Z_s which are shown in Tables 3 and 4 are in reasonably good agreement with the experimental values given in Table 1. The limits of uncertainty in the calculated Z_s, are rather wide because of the large effect of errors in the factor in the exponential, as noted above, and it is thus difficult to attach any physical significance to the discrepancies found here. However, the differences between the calculated and theoretical energies are more significant, and it is probable

Table 4. Theoretical Values of the Configurational Properties of Atoms Adsorbed on Xenon Lattices (Units in Å³/Å², except for energies, which are in deg. K.)

	Square			Triangular		
	$v_1^{(s)}$	Z_s	$(\epsilon_{min}+\epsilon^o)/k$	$v_1^{(s)}$	Z_s	$(\epsilon_{min}+\epsilon^o)/k$
He, 12.5°	.80	7.10^2	-100°	1.80	16.10^2	-100
Ne, 23.2°	.08	18.10^2	-230°	.20	20.10^2	-230
Ar, 79.2°	.04	40.10^2	-910°	.05	20.10^2	-845

that the fact that the calculated energies become increasingly larger than the observed as one progresses from Ar to Ne to He is a consequence of the inaccuracy of the simple combining rule used in this work to obtain the depths of the potential wells for the interactions of the atoms of the adsorbates with xenon atom. Many other more refined combining rules have been proposed which generally give appreciable differences from the rule of the geometric mean only when the differences between the atoms in the pair are large. To take only one example, if one uses the rule suggested by Sams (9), the Ar-Xe well depth is hardly affected, but the Ne-Xe depth is reduced by 15% and the He-Xe depth by 20%. Such reductions in the computed energies shown in Table 3 would evidently give a marked improvement in the agreement between theory and experiment.

Finally, one can estimate the average mutual interactions of pairs of atoms on the surface and the second virial coefficients if it is assumed that the adsorbed atoms are to be found only at the centers of the adsorption sites on the xenon lattices. In this way, the only possible values of the separation distances on the surface are determined by the xenon lattice parameters and the mutual interaction energies are calculable by substituting these distances into the Lennard-Jones functions for the Ar-Ar, Ne-Ne and He-He interactions. Energies calculated in this way are shown in Table 5. Here, w_0 is the estimated repulsive energy for atoms on nearest neighbor sites in the triangular lattice, w_1 is the nearest neighbor attractive energy (next nearest neighbor sites in the triangular case) and w_2 is the energy of atoms on the next distant neighbors. The c_i are the numbers of such pairs of sites per site and are thus coordination numbers for the lattices. Second surface virial coefficients for sitewise adsorption can readily be obtained from these parameters by evaluating the expression

$$\beta_2 = -1 + \sum_i c_i \left(e^{-w_i/kT} - 1\right) \qquad (10)$$

Furthermore, the equation for ϵ_2, the average potential energy of pairs of adsorbed atoms, is also give in terms of these quantities:

$$\epsilon_2 = \sum_i c_i w_i e^{-w_i/kT} \qquad (11)$$

However, values of ϵ_2 calculated from this expression are not quite comparable with the data listed in Table 1,

since these values refer not to the limiting slopes of the q_{st} versus θ plots but rather to the average slopes taken over the region $\theta=0$ to $\theta=.5$. In this case, it is readily shown that Eq. (11) can be replaced by a sum of $c_i w_i$ over the attractive energies only (of course, the limiting slopes and these average slopes will not differ greatly as long as the attractive energies are smaller than kT). Values of β_2 and ϵ_2 calculated for the various adsorbates are also shown in Table 5. Upon comparison with the experimental results, it is evident that the calculations give interaction energies which are too large; in the case of He and Ne, this could be due to the neglect of quantum effects in these calculations of β_2 and ϵ_2. However, it is unlikely that this will affect the calculation for Ar; the discrepancy in this case is probably due either to the use of a Xe-Xe lattice dimension which is too small (which of course would affect all three gases) or to the factor that the perturbation of the potential functions of the pairs of adsorbed atoms by the surface causes an appreciable reduction in the well depth of the effective potential on the surface (this perturbation, which is proportional to polarizability, should be largest for argon) (10).

Table 5. Lateral Interaction Parameters for Pairs of Adsorbed Atoms. (Units of energies are in deg. K.)

	w_0/k, c_0	w_1/k, c_1	w_2/k, c_2	β_2	ϵ_2/k
He, 12.5°, Square	-	$-1.6^{\circ},4$	$-0.2^{\circ},4$	-0.4	-7°
Ne, 23.2°, Square	-	$-9^{\circ},4$	$-1.^{\circ},4$	1	-40°
Ar, 79.2°, Square	-	$-88^{\circ},4$	$-11^{\circ},4$	8	-400°
He, 12.5°, Triangular	$14^{\circ},3$	$-1.6^{\circ},6$	$-0.8^{\circ},3$	-2	-12°
Ne, 23.2°, Triangular	$1000^{\circ},3$	$-9^{\circ},6$	$-4^{\circ},3$	-0.6	-66°
Ar, 79.2°, Triangular	$10000^{\circ},3$	$-88^{\circ},6$	$-44^{\circ},3$	9	-660°

In summary, it has proved possible to make a detailed comparison of the thermodynamic properties of atoms adsorbed on a xenon momolayer at low coverages with theoretical computations. Although such calculations have been frequently reported recently, especially for isolated atoms on graphitized carbon blacks (11), less ambiguity is introduced in the calculations of the properties of rare gases adsorbed on another rare gas than for any other adsorption system known. From the analysis given in this

paper, it appears that the adsorption of He, Ne and Ar on a Xe lattice is essentially sitewise, with the spacings between adsorbate atoms determined primarily by the lattice parameters of the underlying xenon atoms; that the simple geometric mean combining rule gives theoretical energies which are somewhat larger than the experimental, especially when the atoms involved are very different from one another; and that the mutual interactions of atoms on these surfaces are even smaller than those calculated using gas phase potential functions and separations determined from the Xe-Xe spacings. Surprisingly, the calculated properties of atoms adsorbed on a square xenon lattice are not distinctively different from those on the triangular lattice. It was hoped that the helium experiments would provide the crucial test, but fact that the monolayer capacity for helium was not twice that for the other gases does not prove the existence of the square lattice in the light of the calculated repulsive lateral interactions for nearest neighbors in this case as well as for Ne and Ar. The calculated properties of the isolated atoms on the triangular lattice seem to be in somewhat better agreement with experiment than those for the square, but the reverse seems to be true for the properties of pairs of adsorbed atoms. In any case, it does not appear that one can draw any conclusions from this work that are in contradiction to the LEED results which indicate that the xenon monolayer occurs as a slightly distorted triangular array on a graphite surface at low temperatures (3).

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