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Abstract

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STATISTICAL-THERMODYNAMIC CALCULATION OF THE ADSORPTION EQUILIBRIUM OF ARGON ON GRAPHITE

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An important problem in the theory of adsorption is the calculation of adsorption equilibrium on the basis only of the physical properties of the adsorbent and adsorbate ([1,2]). The first and principal stage in solving this problem is the theoretical calculation of the potential energies of adsorbed molecules. The successes achieved in calculations of the adsorption energy of simple and complex nonpolar molecules on graphite and on ionic crystals ([2–6]) make it possible in these cases to solve the problem as a whole, i.e., to calculate the change in the chemical potential of the adsorbate $\Delta\mu$.

Calculations of the "kinetic" factor A in the constant of the BET equation $C = A\exp((E_1 - L)/RT)$ (E_1 is the heat of adsorption in the first layer, L is the heat of condensation) by statistical methods were carried out by Hill and Drenan ([7,8]). However, these calculations refer to an "abstract" adsorbent and are based on functions of the potential energies of adsorbed molecules obtained by integrating the interactions of the atoms of the adsorbed molecules with the atoms of the adsorbent lattice, and not by summing them. We ([9]) calculated the constants C from the equation $C = \exp(\Delta S^0/R) \times \exp(-\Delta U^0/RT)$ (where ΔS^0 and ΔU^0 are the standard changes in the differential entropy and total adsorption energy) for benzene on graphite and on MgO. However, having calculated the adsorption energy in detail, in ([9]) we used a value of ΔS^0 associated with a simplified model of the state of a benzene molecule on the surface of the adsorbent ([10]).

In the present work we have made an approximate calculation of $\Delta\mu$ of argon upon adsorption on the basal face of graphite at small surface coverages θ. Calculations of the potential energy of an argon atom on the basal face of graphite were carried out in a number of works ([2,3,11,12]).

At sufficiently small θ, the partition function for adsorbed molecules Z_a, both for localized and for nonlocalized adsorption, can be written in the form ([13])

$$Z_a = \frac{1}{N_a!} f_a^{N_a}, \tag{1}$$

where N_a is the number of adsorbed molecules, and f_a is the partition function for one adsorbed molecule over the entire surface of the adsorbent. In this case, for transfer of the adsorbate from the standard state in the gas (pressure $p^0 = 760$ mm Hg) to the surface at coverage θ,

$$\Delta\mu = -RT \ln \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \frac{f'_a \omega_m}{kT j_i} \cdot \frac{p^0}{\theta}, \tag{2}$$

where k and h are the Boltzmann and Planck constants; m is the mass of an adsorbate molecule; ω_m is the area occupied by it in a dense monolayer; j_i is the partition function for the internal degrees of freedom of the adsorbate molecule in the gas, with $\theta = N_a \omega_m / s$ and $f'_a = f_a / s$, if s is the surface area.

In calculating f_a, as in ([7,8]), we used the approximation ([14])

$$f = f_{\text{class}} \nu^{**}, \tag{3}$$

where f_{class} is the fully classical partition function,

$$f_{\text{class}} = \frac{1}{h^n} \int \dots \int e^{-H/kT} \, dp_1 \dots dp_n \, dq_1 \dots dq_n \tag{4}$$

(n is the number of degrees of freedom of the molecule, H is the Hamiltonian function for the adsorbate molecule), and

$$\gamma^{**} = f_{\text{harmon. oscill. quant}} / f_{\text{harmon. oscill. class}}, \tag{5}$$

where $f_{\text{harmon. oscill. quant}}$ and $f_{\text{harmon. oscill. class}}$ are the partition functions of harmonic oscillators in the quantum-mechanical and classical forms, respectively, calculated from the shape of the potential-energy surface of the adsorbed molecule near the minimum.

The Hamiltonian function for an adsorbed argon atom is

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \Phi(x, y, z), \tag{6}$$

where p_x, p_y, p_z are the components of momentum; m is the mass of the atom; $\Phi(x, y, z)$ is its potential energy above the basal face of graphite (xy). According to ([2,6])

$$\Phi(x, y, z) = -C_1 \sum_j^{\infty} r_{ij}^{-6} - C_2 \sum_j^{\infty} r_{ij}^{-8} + B \sum_j^{\infty} e^{-r_{ij}/0.28}, \tag{7}$$

where C_1, C_2 are constants of the dispersion interaction; r_{ij} is the distance from the center of the i-th argon atom to the center of the j-th carbon atom of graphite; B is the repulsion constant. The values of the constants C_1, C_2 and of the sums $\sum_j^\infty r_{ij}^{-6}$, $\sum_j^\infty r_{ij}^{-8}$, $\sum_j^\infty e^{-r_{ij}/0.28}$ are given in ([3]). The values of the power sums at a given distance z of the argon atom from the outer plane xy of the centers of the carbon atoms of graphite, and the slopes of the semilogarithmic plots of the dependence of the exponential sums on z, depend only weakly on the position of the point under consideration above the face, i.e., on the coordinates x and y. In order not to complicate the calculations, for the sums $\sum_j^\infty r_{ij}^{-6}$, $\sum_j^\infty r_{ij}^{-8}$ at given values of z, and for the slope of the dependence $\lg \sum_j^\infty e^{-r_{ij}/0.28}$ on z, we took values averaged over three positions c, b, and h: above a carbon atom, above the midpoint of the line joining two nearest atoms, and above the center of the hexagon formed by these atoms. The values of the averaged power and exponential sums, as well as the unaveraged ones ([3]), can, with sufficient accuracy, be expressed respectively by the power functions $p_1 z^{-q_1}$ and $p_2 z^{-q_2}$ and by the exponential function $ke^{-z/l}$, where $q_1 = 3.82$, $p_1 = 5.18 \cdot 10^{16.44}$, $q_2 = 5.94$, $p_2 = 3.80 \cdot 10^{15.48}$, and $l = 0.303 \cdot 10^{-8}$*.

These approximations make it possible to write (7) in the form

$$\Phi(x, y, \alpha) = u_{o1}(x, y)\alpha^{-q_1} + u_{o2}(x, y)\alpha^{-q_2} +$$

$$+ u_{op}(x, y) \exp\left\{-\frac{(\alpha - 1)z_0(x, y)}{l}\right\}, \tag{8}$$

where

$$u_{o1}(x, y) = -C_1 p_1 z_0^{-q_1}, \qquad u_{o2}(x, y) = -C_2 p_2 z_0^{-q_2},$$

$$u_{op}(x, y) = Bke^{-z_0/l} = -\frac{l}{z_0}\left[u_{o1}q_1 + u_{o2}q_2\right], \qquad \alpha = \frac{z}{z_0}. \tag{9}$$

* In ([3]), in the first column of Table 7, the letters b and h were inadvertently interchanged.

The equilibrium distance of the center of an argon atom from the first plane of centers of carbon atoms of the lattice is

$$z_0 = \sqrt{r_e^2 - (x_C - x)^2 - (y_C - y)^2}, \tag{10}$$

where x, y are the coordinates of the center of the argon atom; x_C, y_C are those of the nearest carbon atom; r_e is the equilibrium distance between the centers of the argon atom and the nearest carbon atom, which we took (3) to be equal

to the sum of the van der Waals radii of the argon atom (1.91 Å) and of the carbon atom in graphite (1.70 Å).

Substitution of (8) and (6) into (4) and integration over the momentum components gives (7)

$$f_{\text{class}} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{2s}{3a^2\sqrt{3}} \iiint \exp\left(-\frac{\Phi(x,y,\alpha)}{kT}\right) \operatorname{erf}\left(-\frac{\Phi}{kT}\right)^{1/2} z_0\, dx\, dy\, d\alpha, \tag{11}$$

where $3a^2\sqrt{3}/2$ is the area of the hexagon formed by the carbon atoms of the basal face ($a = 1.418$ Å is the lattice constant of graphite);

Table 1

Position x	Position y	z_0	$I(x,y)$	Position x	Position y	z_0	$I(x,y)$
0	0	3.32	0.262	$a/8$	$a\sqrt{3}/8$	3.45	0.0300
0	$a\sqrt{3}/8$	3.42	0.0462	$a/4$	$a\sqrt{3}/4$	3.54	0.0081
0	$a\sqrt{3}/4$	3.49	0.0175	$3a/8$	$a\cdot 3\sqrt{3}/8$	3.59	0.0043
0	$a\cdot 3\sqrt{3}/8$	3.53	0.0095	$a/2$	$a\sqrt{3}/2$	3.61	0.0036
0	$a\sqrt{3}/2$	3.54	0.0081	$a/4$	$a\sqrt{3}/2$	3.59	0.0043

$\operatorname{erf}(-\Phi/kT)^{1/2}$ is the probability integral. Integration over x and y in (11) is carried out within the limits of one hexagon. The value of the integral in (11) was calculated graphically. Table 1 gives the results $I(x,y)$ of such integration over α for different positions over this hexagon at $T = 77.8$°K (the origin of coordinates coincides with the center of the hexagon, and the x axis passes through the center of a carbon atom). The integration was performed for those values of α for which the potential energy of the adsorbed atom $\Phi(x,y,\alpha) \leq 0$ (7). The value of $\exp(-\Phi(x,y,\alpha)/kT)$ for argon on graphite decreases rapidly when α deviates from unity. Since within the limits of α over which the integration was carried out the value of the factor $\operatorname{erf}(-\Phi/kT)^{1/2}$ is practically equal to unity, we neglected it. Integration over x and y within the limits of one hexagon gave the value $J = 0.034a^2$ ($T = 77.8°$).

The quantum-mechanical factor ν^{**} (5) in the case of an argon atom above the graphite surface is

$$\nu^{**} = \left(\frac{h\nu_x}{kT}\right)\left[1 - \exp\left(\frac{h\nu_x}{kT}\right)\right]^{-1} \times$$

$$\times \frac{h\nu_y}{kT}\left[1-\exp\left(-\frac{h\nu_y}{kT}\right)\right]^{-1}\frac{h\nu_z}{kT}\left[1-\exp\left(-\frac{h\nu_z}{kT}\right)\right]^{-1}, \qquad (12)$$

where ν_x, ν_y, and ν_z are the frequencies of oscillation of the adsorbed argon atom along the corresponding axes near the potential minimum (above the center of the hexagon and for $z = z_0$). Calculating the frequencies of oscillation,

$$\nu_x = \frac{1}{2\pi}\sqrt{\frac{K_x}{m}}, \qquad \nu_y = \frac{1}{2\pi}\sqrt{\frac{K_y}{m}}, \qquad \nu_z = \frac{1}{2\pi}\sqrt{\frac{K_z}{m}}, \qquad (13)$$

the constants K_x, K_y, and K_z were estimated analytically from

$$K_x = \left(\frac{\partial^2\Phi}{\partial x^2}\right)_{x=0,\ y=0,\ z=z_0}, \qquad K_y = \left(\frac{\partial^2\Phi}{\partial y^2}\right)_{x=0,\ y=0,\ z=z_0}, \qquad K_z = \left(\frac{\partial^2\Phi}{\partial z^2}\right)_{x=0,\ y=0,\ z=z_0} \qquad (14)$$

from (8), (9), and from a suitable approximation to (10). In this case $\nu_x \approx \nu_y = 5\cdot 10^{11}$—$11\cdot 10^{11}$ sec^{-1} and $\nu_z = 1.5\cdot 10^{12}$ sec^{-1},* whence $\nu^{**} \approx 2$.

The magnitude ω_m depends on the packing of the argon atoms over the surface. We used the values given in (16) for ω_m for hexagonal and square packings, equal to 12.8 and 14.7 Å^2. The state functions j_i for the internal degrees of freedom of an argon atom in the gas and adsorbed phases were taken to be identical.

Substituting the corresponding expressions and values into (2), we obtained the following expressions for the dependence of $\Delta\mu$ on θ upon transition of argon from the gas at $p^0 = 760$ mm Hg to the surface of the basal face of graphite at $T = 77.8°$K:

$$\Delta\mu = -1.2_5 + 0.355\lg\theta \text{ kcal/mole} \qquad (\omega_m = 12.8 \text{ Å}^2); \qquad (15)$$

$$\Delta\mu = -1.3_0 + 0.355\lg\theta \text{ kcal/mole} \qquad (\omega_m = 14.7 \text{ Å}^2). \qquad (16)$$

Thus, $\Delta\mu$ for argon depends only weakly on the value of ω_m. In Fig. 1 the initial portions of the experimental and calculated curves for the dependence of $-\Delta\mu$ on θ are compared. Experimental curve 1 was calculated from the adsorption isotherm measured in (16), using the thermodynamic formula $-\Delta\mu = RT\ln 760/p(\theta)$. Calculated curve 2 lies close to the experimental one.** Thus, on the basis of theoretical calculations of the adsorption energy, the statistical method makes it possible, to a satisfactory approximation, to calculate the change in the chemical potential of argon upon transition from the gas phase to the adsorbed state for small coverages of the graphite surface.

Fig. 1

Figure 1: Fig. 1

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* In (15) an approximate value $\nu_z = 1.19 \cdot 10^{12}$ sec^{-1} was calculated.

** At higher θ, the experimental curve shows the influence of interaction between adsorbed molecules, which has not yet been taken into account by us in the calculated curve (the energy of this interaction was calculated in (12)).

Note: Figure translations are in progress. See original paper for figures.