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Abstract

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

(Presented by Academician A. N. Frumkin on 18 III 1961)

The calculation we carried out ([1]) of the change in the chemical potential $\Delta\mu$ of argon on transfer from the gas to the surface of graphite showed that, by a statistical method, based on the theoretical calculation of the potential energy of adsorption, it is possible, to a satisfactory approximation, to calculate $\Delta\mu$ for monatomic molecules at small surface coverages θ. In the present work a calculation has been made of $\Delta\mu$ for the polyatomic benzene molecule upon adsorption on graphite.

At sufficiently small θ, for both localized and nonlocalized adsorption ([2,1]),

$$\Delta\mu = -RT \ln \frac{f_a/N_a}{f/N}, \tag{1}$$

where f_a, f and N_a, N are the state functions and the numbers of molecules in the adsorbed layer and in the gas. According to the approximation ([3])

$$f_a = f_{a\,\text{class}} \nu^{**}, \tag{2}$$

where

$$f_{a\,\text{class}} = \frac{1}{h^n} \int \cdots \int e^{-H/kT}\, dp_1 \cdots dp_n dq_1 \cdots dq_n \tag{3}$$

(n is the number of degrees of freedom of the adsorbate molecule, H is the Hamiltonian function; p_n and q_n are components of momentum and coordinates), and

$$\nu^{**} = f_{\text{harm. osc. quant.}}/f_{\text{harm. osc. class}}, \tag{4}$$

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

For an adsorbed benzene molecule ([4,5])

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \frac{p_\vartheta^2}{2A} + \frac{(p_\varphi - p_\psi \cos\vartheta)^2}{2A \sin^2\vartheta} + \frac{p_\psi^2}{2C} + \Phi, \tag{5}$$

where m is the mass of the molecule; A and C are its moments of inertia, respectively with respect to a diameter and with respect to the axis perpendicular to the plane of the benzene ring and passing through its center; $p_x, p_y, p_z, p_\varphi, p_\vartheta, p_\psi$ are components of momentum; x, y, z are the Cartesian coordinates of the center of the benzene molecule (the plane $x, y, z = 0$ passes through the centers of the carbon atoms of the basal face of graphite); φ, ϑ, ψ are the usual Euler angles, and $\Phi = \Phi(x, y, z, \varphi, \vartheta, \psi)$ is the potential energy of the adsorbed benzene molecule. We obtained the function Φ by summing the potential energies of interaction of the force centers of the benzene molecule with the force centers of the adsorbent.* We neglected the potential energy of interaction between adsorbed molecules.**

* In ([4]), Φ was obtained by integrating the interaction energy of the volume elements of the benzene molecule with the volume elements of the graphite lattice.

** Measurements of the differential heats of adsorption of benzene on graphitized thermal blacks with a homogeneous surface showed that the energy of interaction adsorbate-adsorbate in the case of benzene is indeed small ([6]).

Calculations of Φ for different positions of a benzene molecule above the basal face of graphite and different z at $\vartheta = 0$ [7,8] showed that, for a given z and $\vartheta = 0$, Φ depends only weakly on the position of the benzene molecule. In the present work we neglected the dependence of Φ and of the equilibrium distance z_0 on x, y, and φ. In deriving the dependence of Φ on z, ϑ, and ψ, we considered the benzene molecule as a regular plane hexagon, at whose vertices are located the force centers i—the CH groups. For the dependence of the potential energy Φ_i of interaction of center i (the CH group) of the adsorbate with the entire lattice of the adsorbent on z_i, the expression [1] was adopted

$$\Phi_i = u_{01}\alpha_i^{-q_1} + u_{02}\alpha_i^{-q_2} + u_{0\rho}e^{-(\alpha_i - 1)z_{i0}/l}, \tag{6}$$

where

$$u_{01} = -C_{1i}p_1 z_{i0}^{-q_1}, \qquad u_{02} = -C_{2i}p_2 z_{i0}^{-q_2}, \tag{7}$$

$$u_{0\rho} = B_i k e^{-z_{i0}/l} = -\frac{l}{z_{i0}}(u_{01}q_1 + u_{02}q_2), \qquad \alpha_i = z_i/z_{i0}.$$

The constants of dispersion attraction for the benzene molecule $C_1 = 6C_{1i}$ and $C_2 = 6C_{2i}$ were calculated in [7] (respectively by the Kirkwood-Müller formula [9]) and by an analogous formula [10,7], and the constants p_1, q_1, p_2, q_2, and l– in [1]. For CH, z_{i0} was taken equal to the sum of the effective van der Waals radius of CH (1.85 Å, i.e., one-half of the van der Waals thickness of the benzene molecule) and one-half of the interplanar spacing of the lattice (1.70 Å), i.e., equal to 3.55 Å.

The energy Φ is found by summing the Φ_i:

$$\Phi(\alpha, \beta, \psi) = u_{01}\sum_{i=1}^{6}(\alpha+\beta\sin\psi_i)^{-q_1} + u_{02}\sum_{i=1}^{6}(\alpha+\beta\sin\psi_i)^{-q_2} + u_{0\rho}\sum_{i=1}^{6}e^{-(\alpha+\beta\sin\psi_i-1)z_{i0}/l}, \tag{8}$$

where

$$\alpha = z/z_{i0}; \qquad \beta = \frac{d}{z_{i0}}\sin\vartheta^*; \qquad \psi_i = (i-1)\frac{\pi}{3} + \psi. \tag{9}$$

Substitution of (5) into (3), integration, and allowance for the symmetry number of the molecule σ and for the state function of its internal vibrations j_v lead to expression (4):

$$f_{a\,\mathrm{class}} = \frac{1}{\sigma} j_v\, 2\pi \left(\frac{2\pi mkT}{h^2}\right)^{3/2} s\, \frac{2\pi AkT}{h^2} \left(\frac{2\pi CkT}{h^2}\right)^{1/2} \frac{2z_0^2}{d}\, Q, \tag{10}$$

where

$$Q = \int_0^{2\pi} d\psi \int_0^{d/z_{i0}} \frac{\beta\, d\beta}{[(d/z_{i0})^2 - \beta^2]^{1/2}} \int_{\Phi\le 0} \exp\left(-\frac{\Phi}{kT}\right) \mathrm{erf}\left(-\frac{\Phi}{kT}\right)^{1/2} d\alpha, \tag{11}$$

and s is the surface area of the adsorbent. The value of integral (11) was calculated graphically; the results are given in Table 1. As can be seen from the table, the subinte–

* The distance of the center of the CH group from the center of the hexagon of carbon atoms, d, was estimated from the relation [4]

$$d = r_{\mathrm{C-C}} + r_{\mathrm{C-H}} \frac{\Phi_{0\mathrm{H}}}{\Phi_{0\mathrm{H}} + \Phi_{0\mathrm{C}}} \simeq 1.87 \text{ Å},$$

where $r_{C-C} = 1.39$ Å is the C–C bond length; $r_{C-H} = 1.08$ Å is the C–H bond length; Φ_{0H} and Φ_{0C} are the potential energies of interaction of the H and C atoms of the molecule with the basal face of graphite at $z_i = z_{i0}$ (z_i is the distance of force center i from the x, y plane, $z = 0$; z_{i0} is the corresponding equilibrium distance). Φ_{0H} and Φ_{0C} were estimated from formulas (6) and (7). It was assumed that the polarizability α_{CH} and the diamagnetic susceptibility χ_{CH} of the aromatic CH group are additively composed of the α and χ of the C and H atoms, and that the ratios α_C/α_H and χ_C/χ_H in the aromatic CH group are equal to the corresponding ratios in the aliphatic CH group. For the H and C atoms of the benzene molecule, z_{i0} were taken equal to 2.90 and 3.55 Å.

Table 1

Results of calculating integral (11) for a benzene molecule on the surface of graphite at

$$T = 293^{\circ}\mathrm{K}; \quad f(\beta,\psi) = \int \exp\left(-\frac{\Phi}{kT}\right) \operatorname{erf}\left(-\frac{\Phi}{kT}\right)^{1/2} d\alpha$$

and

$$f(\psi) = \int_0^{d/z_{i0}} \frac{f(\beta,\psi)\,\beta\,d\beta}{\left[\left(\frac{d}{z_{i0}}\right)^2 - \beta^2\right]^{1/2}}.$$

β	$\dfrac{\beta}{[(d/z_{i0})^2-\beta^2]^{1/2}}$	$\psi = 0^{\circ}$: $f(\beta,\psi)$	$\psi = 0^{\circ}$: $\dfrac{f(\beta,\psi)\beta}{[(d/z_{i0})^2-\beta^2]^{1/2}}$	$\psi = 30^{\circ}$: $f(\beta,\psi)$	$\psi = 30^{\circ}$: $\dfrac{f(\beta,\psi)\beta}{[(d/z_{i0})^2-\beta^2]^{1/2}}$
0	0.00	$2.21 \cdot 10^6$	0.00	–	–
0.025	0.0475	$1.92 \cdot 10^6$	$0.0912 \cdot 10^6$	–	–
0.050	0.0953	$1.53 \cdot 10^6$	$0.146 \cdot 10^6$	–	–
0.100	0.1934	$0.556 \cdot 10^6$	$0.108 \cdot 10^6$	$0.556 \cdot 10^6$	$0.108 \cdot 10^6$
0.20	0.4103	$0.049 \cdot 10^6$	$0.020 \cdot 10^6$	–	–
0.30	0.6926	$0.0072 \cdot 10^6$	$0.0050 \cdot 10^6$	$0.0063 \cdot 10^6$	$0.0044 \cdot 10^6$
0.50	3.008	$0.00079 \cdot 10^6$	$0.0024 \cdot 10^6$	$0.00045 \cdot 10^6$	$0.0014 \cdot 10^6$
		$f(\psi) = 0.185 \cdot 10^5$		$f(\psi) = 0.185 \cdot 10^5$	

The integral function $f(\psi)$ is practically independent of ψ. Hence $Q = 2\pi 0.185 \cdot 10^5$ and $f_{a\,\mathrm{class}} = 0.74 \cdot 10^{29} s j_\sigma/\sigma$.

Further, in our case (4)

Figure 1

Figure 1: Figure 1

$$\nu^{**} = (h\nu_z/kT)(h\nu_\vartheta/kT)^2 \left[1 - \exp(-h\nu_z/kT)\right]^{-1} \left[1 - \exp(-h\nu_\vartheta/kT)\right]^{-2}, \quad (12)$$

where ν_z is the frequency of vibration of the center of the benzene molecule perpendicular to the surface, and ν_ϑ is the frequency of its torsional vibrations. Near the potential minimum

$$\Phi = \Phi_{\substack{z=z_{i0} \\ \vartheta=0}} + \frac{3D}{z_{i0}^2}(z - z_{i0})^2 + \frac{3}{2}\frac{Dd^2}{z_{i0}^2}\vartheta^2, \quad (13)$$

where

$$D = u_{01}q_1(q_1 + 1) + u_{02}q_2(q_2 + 1) + u_{0p}\frac{z_{i0}^2}{l^2}. \quad (14)$$

Hence

$$\nu_z = \frac{1}{2\pi z_{i0}}\sqrt{\frac{6D}{m}} = 2.08 \cdot 10^{12}\ \text{sec}^{-1}, \quad (15)$$

$$\nu_\vartheta = \frac{d}{2\pi z_{i0}}\sqrt{\frac{3D}{A}} = 2.55 \cdot 10^{12}\ \text{sec}^{-1}. \quad (16)$$

Fig. 1. Dependence of the change in the chemical potential of benzene on the filling of the graphite surface at 20°; **1** —calculated from experiments with graphitized carbon black, **2** —calculated theoretically.

Substituting these values into (12) and (2), we obtain $\nu^{**} = 1.8$ and $f_a = 1.33 \cdot 10^{29} s j_\sigma/\sigma$.

The partition function for a benzene molecule in the gas phase ($\Phi = 0$)

$$f = \frac{j_v}{\sigma}\, 8\pi^2 \left(\frac{2\pi mkT}{h^2}\right)^{3/2} v \left(\frac{2\pi AkT}{h^2}\right) \left(\frac{2\pi CkT}{h^2}\right)^{1/2}, \quad (17)$$

where v is the volume of the gas. Substitution of (17) and (10), taking (2) into account, into (1), under the assumption that σ and j_v do not change upon adsorption, gives

$$\Delta\mu = -RT \ln \frac{z_{i0}^2 Q \nu^{**} p^0 \omega_m}{dkT} + RT \ln \theta, \tag{18}$$

where $p^0 = 760$ mm Hg is the standard gas pressure; $\omega_m = 40$ Å^2 ([11,6]) is the area occupied by a benzene molecule in a dense monolayer, and $\theta = \omega_m / s / N_a$.

Substituting the corresponding values in (18), we obtain, for the transfer of benzene from the gas at 760 mm to the surface of the basal face of graphite at 293°K,

$$\Delta\mu = -3.15 + 1.34 \lg \theta \text{ kcal/mole}. \tag{19}$$

In Fig. 1 the initial portions of the experimental and calculated dependences $-\Delta\mu$ on θ are compared. Experimental curve 1 was calculated from the adsorption isotherm obtained in [6], using the thermodynamic formula $-\Delta\mu = RT \ln 760/p(\theta)$. Calculated curve 2 lies close to the experimental one. Thus, also in the case of a polyatomic molecule, the complete theoretical calculation gave values of $\Delta\mu$ close to the experimental ones.

Table 2

Results of approximate calculations

No.	Character of the approximations	$f_{a\,\text{class}}/10^{29} S j_\sigma$	Error in $f_{a\,\text{class}}$	Error in $\Delta\mu$, kcal/mole
1	The most rigorous variant: the form $\Phi = \Phi(z, \vartheta, \psi)$ is given by expression (8)	0.74	0	0

No.	Character of the approximations	$f_{a\,\text{class}}/10^{29}Sj_{\sigma}$	Error in $f_{a\,\text{class}}$	Error in $\Delta\mu$, kcal/mole
2	Motion perpendicular to the surface is a harmonic vibration and Φ does not depend on ψ:$\Phi(z,\vartheta) = \Phi(z,\vartheta)_{z=z_0} + \frac{k_z(\vartheta)}{2}(z - z_0)^2$	0.72	3%	0.016
3	As in variant 2, but it is assumed that $k_z \neq f(\vartheta)$, and is equal to its value at $\vartheta = 0$	0.68	9%	0.05
4	Harmonic vibration perpendicular to the surface, and harmonic torsional vibrations:$\Phi(z,\vartheta) = \Phi_{\substack{z=z_0\\ \vartheta=0}} + \frac{k_z(z-z_0)^2}{2} + \frac{k_\theta}{2}\vartheta^2$	0.23	by a factor of 3.2	0.68

No.	Character of the approximations	$f_{a\,\text{class}}/10^{29}Sj_\sigma$	Error in $f_{a\,\text{class}}$	Error in $\Delta\mu$, kcal/mole
5	Harmonic vibration perpendicular to the surface and free rotation$\Phi(z) = \Phi_{\substack{z=z_0\\ \vartheta=0}} + \frac{k_z(z-z_0)^2}{2}$	44.5	by a factor of 60	2.4

Let us now consider some other variants of the approximate calculation. In Table 2 the result of calculating $f_{a\,\text{class}}$ with expression (8) for Φ is compared with the results of calculations of $f_{a\,\text{class}}$ for various assumptions about the state of the benzene molecule at the graphite surface. Also given are the errors in $f_{a\,\text{class}}$ and in $\Delta\mu$ arising under these assumptions, relative to the corresponding values of the first calculation variant. The table shows the admissibility of approximations Nos. 2 and 3, which greatly facilitates the calculations.

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