Thermodynamic parameters of excess and absolute adsorption of CH_4 and SF_6 on carbons

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Isosteres, isosteric heats, and heat capacities of methane and sulfur hexafluoride on carbons with different porosities were calculated to characterize the excess adsorption and absolute adsorption. The nonlinear character of isosteres of excess adsorption and absolute adsorption of sulfur hexafluoride on FAS carbon with developed mesoporosity was shown.

Key words: adsorption, isostere, adsorption heat, partial thermal capacity of adsorbate.

To describe adsorption systems and design adsorption units, equilibrium, kinetic, and thermodynamic parameters of these systems are required. Such thermodynamic properties as adsorption heats and heat capacities of the adsorbed molecules can directly be measured by calorimetry or calculated from the measured adsorption isotherms.

The isotherms of absolute adsorption or isotherms of the total amount adsorbed can be measured only for a restricted number of adsorption systems. Therefore, the isotherm of excess adsorption is obtained experimentally and used for calculation of excess thermodynamic properties. The thermodynamics of gas and vapor adsorption at low pressures of adsorptives has been considered previously.[1,2] For gas and vapor adsorption, the plots of excess adsorption ($\ln P$) *vs.* $1/T$ (isosteres) are virtually linear over a region of low pressures in a wide temperature range. In this case, the isosteric heats of excess adsorption and calculated differential heat capacities of adsorbed substances are in good agreement with calorimetric data.[3] At elevated pressures (>10 MPa) and high temperatures, the shape of the isosteres of excess adsorption noticeably differs from linearity, and the calculated isosteric heats even converge at indefinite values.[4,5] A change in the slope to the isostere plotted in the coordinates $\ln P$—$1/T$ can serve as a quantitative estimation of the deviation of the isostere from linearity.

In this work, we examined the isosteres, isosteric heats, and heat capacities of methane and sulfur hexafluoride for excess and absolute adsorption. The measurements were performed in a wide pressure range on carbon adsorbents with different porosities. We also attempted to consider the deviation of the isosteres from linearity from the viewpoint of statistical thermodynamics.

Experimental

The excess adsorption isotherms of CH_4 (at P = 0.001—160 MPa) were measured at four temperatures in the 313—408 K range, and the adsorption isotherms of SF_6 (at P = 0.001—2.4 MPa) were measured at six temperatures in the 298—408 K interval on the microporous carbon CMS with a surface area of mesopores S_{me} = 28 m^2 g^{-1} and on carbon FAS with developed mesoporosity (S_{me} = 86 m^2 g^{-1}).[6]

The adsorption volumes were found for all systems under study using the correlation between the experimentally measured excess adsorption (Γ) and total content or absolute adsorption (a), $a = \Gamma + \rho_g W$ (W is the adsorption volume, and ρ_g is the density of the equilibrium gaseous phase). For the adsorption systems CMS—CH_4 and FAS—CH_4, the adsorption volumes calculated by our method[7] amounted to 0.24±0.015 and 0.20±0.03 cm^3 g^{-1}, respectively. For the CMS—SF_6 and FAS—SF_6 systems, the volume of micropores was determined by the Dubinin—Radushkevich (DR) method. The volume of the micropores for CMS—SF_6 was 0.197 cm^3 g^{-1}. When sulfur hexafluoride was adsorbed on FAS carbon, the main part of the micropores remained inaccessible for large SF_6 molecules, and the volume of micropores was as low as 0.014 cm^3 g^{-1}. The adsorption volume of the mesoporous system for FAS carbon was also determined, using the Frenkel—Halsey—Hill (FHH) isotherm equation.[8] The FHH equation was also used to calculate the thickness of the adsorption layer z. Taking into account the known value of the mesopore surface S_{me}, the adsorption volume of the mesoporous carbon structure was determined. This volume was equal to 0.04 cm^3 g^{-1}, and the total adsorption volume of this system was 0.054 cm^3 g^{-1}.

Based on the above adsorption volumes, the families of absolute adsorption isotherms were plotted for all systems under study. From the isotherms the corresponding families of absolute adsorption isosteres were plotted. Figures 1 and 2 show isosteres of absolute adsorption of SF_6 on CMS and FAS carbons, whereas isosteres of CH_4 on the same carbons are omitted because they are linear and similar to those presented in Fig. 1.

Results and Discussion

Thermodynamic parameters of excess adsorption. The excess adsorption isosteres were calculated from the families of isotherms determined for the excess adsorption of CH_4, and SF_6 on samples of active carbon (Figs. 3 and 4). For FAS carbon (see Fig. 3) the isosteres of CH_4, which lie above the critical temperature (T_c = 190.77 K) and involve corresponding pressures,

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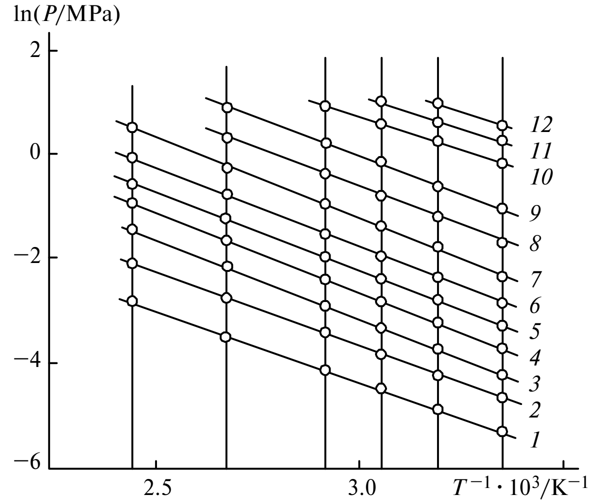

Fig. 1. Isosteres of absolute adsorption of SF_6 on CMS carbon: 0.2 (*1*), 0.4 (*2*), 0.6 (*3*), 0.8 (*4*), 1.0 (*5*), 1.2 (*6*), 1.4 (*7*), 1.6 (*8*), 1.8 (*9*), 2.0 (*10*), 2.10 (*11*), and 2.20 mmol g^{-1} (*12*).

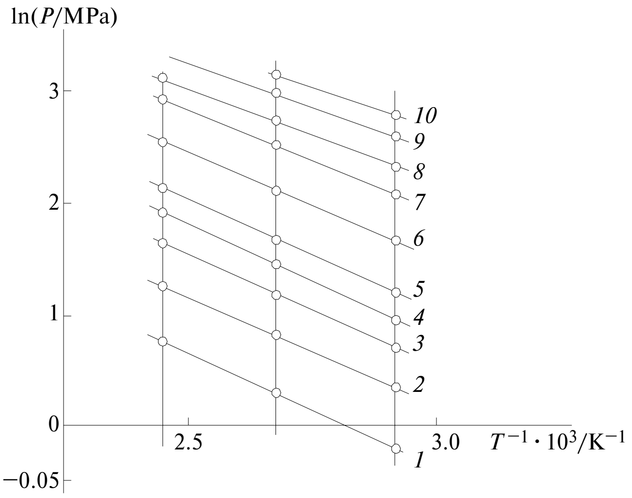

Fig. 3. Isosteres of excess adsorption of CH_4 on FAS carbon: 0.2 (*1*), 0.3 (*2*), 0.4 (*3*), 0.5 (*4*), 0.6 (*5*), 0.8 (*6*), 1.0 (*7*), 1.1 (*8*), 1.2 (*9*), and 1.3 mmol g^{-1} (*10*).

are almost linear for coverages of up to 1.3 mmol g^{-1}. For methane adsorption on the microporous CMS carbon (see Fig. 4), the isosteres are also linear over the same region of coverages, but as values of the adsorbed amount and temperature increase the absolute value of the tangent slope to the isostere increases noticeably, and the isosteres display a nonlinearity. At Γ = 1.9 mmol g^{-1} the slope to the isostere (see Fig. 4, curve *12*) at point *A* takes the opposite sign and converges to infinity. This implies that the adsorption process changes from exothermic to endothermic. For this isotherm the amount adsorbed (Γ = 1.9 mmol g^{-1}) corresponds to Γ_{max} at $T \approx 410$ K.

When sulfur hexafluoride is adsorbed on the microporous carbon CMS (Fig. 5), the excess adsorption isosteres are virtually linear at almost all coverages over the temperature range used, and only when the amounts adsorbed are ≥1.8 mmol g^{-1} do the temperature plots of

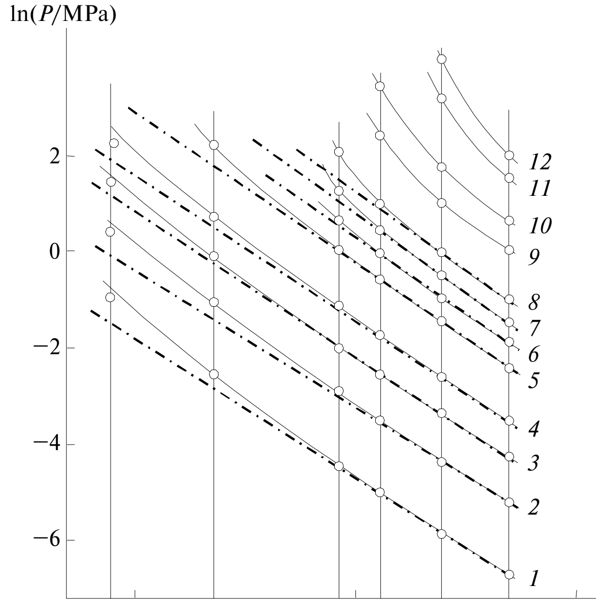

Fig. 2. Isosteres of absolute adsorption of SF_6 on FAS carbon: 0.02 (*1*), 0.03 (*2*), 0.04 (*3*), 0.05 (*4*), 0.07 (*5*), 0.08 (*6*), 0.09 (*7*), 0.10 (*8*), 0.12 (*9*), 0.13 (*10*), 0.15 (*11*), and 0.16 mmol g^{-1} (*12*).

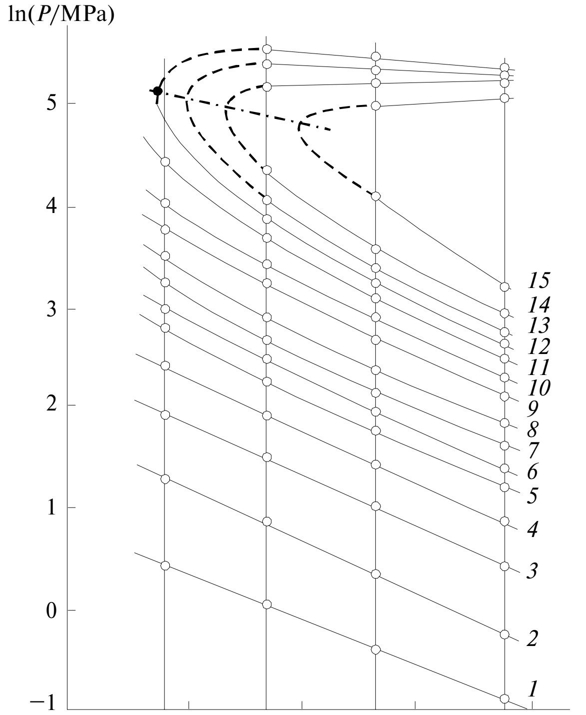

Fig. 4. Isosteres of excess adsorption of CH_4 on CMS carbon: 0.1 (*1*), 0.3 (*2*), 0.5 (*3*), 0.7 (*4*), 0.9 (*5*), 1.0 (*6*), 1.15 (*7*), 1.3 (*8*), 1.5 (*9*), 1.65 (*10*), 1.8 (*11*), 1.9 (*12*), 2.0 (*13*), 2.1 (*14*), and 2.3 mmol g^{-1} (*15*).

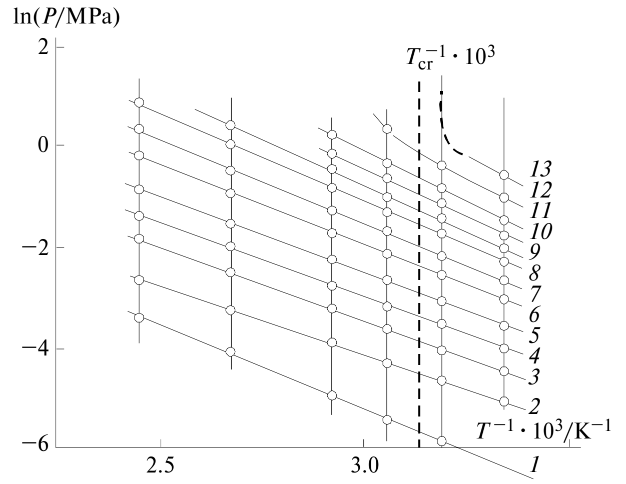

Fig. 5. Isosteres of excess adsorption of SF_6 on CMS carbon: 0.1 (*1*), 0.25 (*2*), 0.5 (*3*), 0.65 (*4*), 0.85 (*5*), 1.1 (*6*), 1.25 (*7*), 1.4 (*8*), 1.5 (*9*), 1.6 (*10*), 1.7 (*11*), 1.8 (*12*), and 1.9 mmol g^{-1} (*13*).

the isosteres become nonlinear. This agrees well with the model that assumes that initial adsorption involves micropores with a surface area close to that of the total adsorbent surface (S_{tot} = 710 m^2 g^{-1}). With further adsorption mesopores are filled. However, these mesopores have a small surface area and CMS carbon adsorbs insignificant amounts of sulfur hexafluoride.

A different situation is observed for SF_6 adsorption on FAS carbon (Fig. 6). First, adsorption of sulfur hexafluoride at the highest points of the adsorption isotherms at T = 298 K is approximately an order of magnitude lower than that on CMS carbon. At the same time, the adsorption values of methane on these carbons are close (T = 373 K, $P \approx$ 11 MPa). They correlate well with the surface area of the sorbents S_{tot}(CMS) and S_{tot}(FAS).[6] The adsorbed amounts of CH_4 and SF_6 (Γ) on CMS and FAS carbons and the surface areas of the sorbents are presented below.

Carbon	Γ/mmol g^{-1}		S_{tot}/m^2 g^{-1}
	CH_4 (373 K)	SF_6 (298 K)	
CMS	2.19	~2	710
FAS	2.07	~0.2	690

Second, the linearity of the excess adsorption isosteres on FAS carbon is observed only at lower temperatures (298—327 K) and lower coverages of up to ~0.1 mmol g^{-1} (see Fig. 6). It has previously been shown[6] that the amounts of SF_6 adsorbed in the microporous and mesoporous parts of FAS carbon are approximately equal, and the surface areas determined from SF_6 are as follows: S_{me} = 9.9 m^2 g^{-1} and S_{tot} = 22 m^2 g^{-1}.

The specific features of the behavior of the excess adsorption isosteres of various gases on carbons and zeolites[5,9,10] suggest the following. First, the excess adsorption isosteres always have a region where the nonlinearity is so high that the slope of the isostere converges to infinity. Second, for adsorbents with commensurable volumes of micropores and mesopores, the region of isosteric nonlinearity is shifted toward lower temperatures and reduced adsorption.

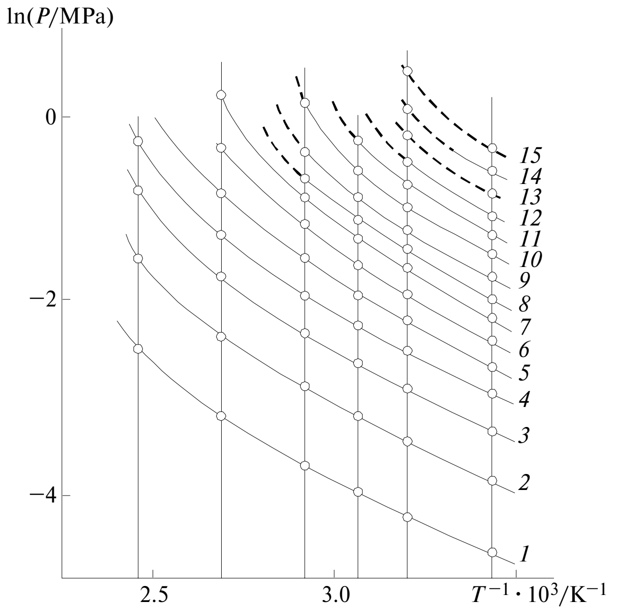

Fig. 6. Isosteres of excess adsorption of SF_6 on FAS carbon: 0.01 (*1*), 0.02 (*2*), 0.03 (*3*), 0.04 (*4*), 0.05 (*5*), 0.06 (*6*), 0.07 (*7*), 0.08 (*8*), 0.09 (*9*), 0.10 (*10*), 0.11 (*11*), 0.12 (*12*), 0.13 (*13*), 0.14 (*14*), and 0.15 mmol g^{-1} (*15*).

The isosteric heats q_{st} of adsorption of these substances were calculated from the excess adsorption isosteres by the equation[2]

$$q_{st} = -Tv_g(\partial P/\partial T)_\Gamma, \qquad (1)$$

where v_g is the molar volume of the gas in the equilibrium gaseous phase.

The initial heats of the excess adsorption were determined from the temperature plot of Henry's constants (K) (Fig. 7). The plot shows that a linear relation of ln$K$ to $1/T$ is observed for all studied systems. Note that the plots of ln$K$ *vs.* $1/T$ for the CH_4—FAS and CH_4—CMS systems almost coincide, and for adsorption of SF_6 on the same carbons the slopes of the straight lines are also similar. It follows from the obtained plots of ln$K$ *vs.* $1/T$ that the initial heats of adsorption of methane on FAS and CMS are equal to 16 kJ mol^{-1}, and the initial heats of adsorption of SF_6 on these carbons are 23 kJ mol^{-1}. The initial heats of adsorption of methane and sulfur hexafluoride on CMS and FAS coincide because the sorbed molecules first enter the narrowest pores where the sorption field is extremely strong. The initial heat of adsorption for sulfur hexafluoride is higher than that for methane. When methane and sulfur hexafluoride are adsorbed on carbon adsorbents where electric fields are absent, the initial heat of adsorption is associated with the energy of dispersion interaction (E) of the sorbed molecules with the adsorbent atoms. Due to this, the difference between the adsorption heats of methane and

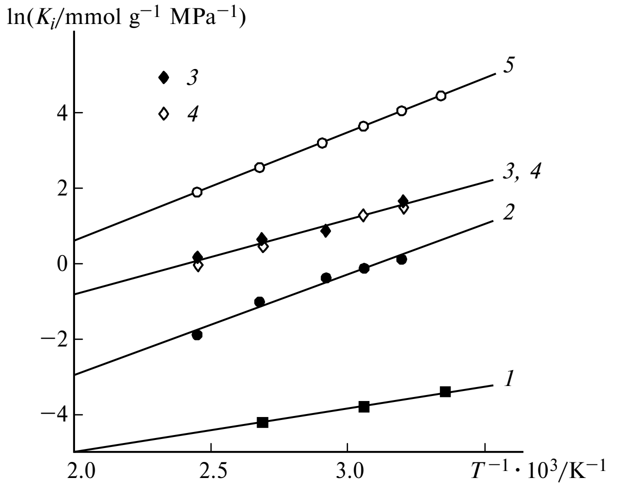

Fig. 7. Temperature relations of Henry's constants: SF_6—carbon black (*1*), SF_6—FAS (*2*), CH_4—CMS (*3*), CH_4—FAS (*4*), and SF_6—CMS (*5*).

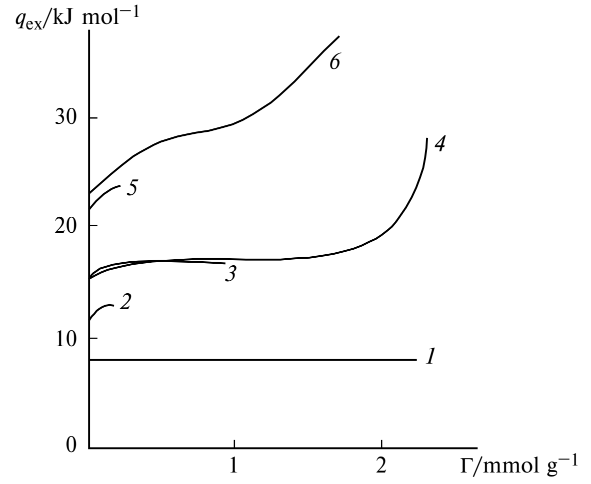

Fig. 8. Condensation heat of SF_6 (*1*) and isosteric heats of excess adsorption (q_{ex}): SF_6—carbon black (*2*), CH_4—FAS (*3*), CH_4—CMS (*4*), SF_6—FAS (*5*), and SF_6—CMS (*6*).

sulfur hexafluoride on the same sample is related to the nature of adsorbed molecules. The constant of dispersion attraction (C_6) depends on the polarizability (α_a) and magnetic susceptibility (χ_a) of methane or sulfur hexafluoride molecules and on α_b and χ_b of the carbon sorbent atoms,[11,12] which can be considered equal for these adsorbates. The calculation gives C_6 equal to −0.385 and −0.269 for SF_6 and CH_4, respectively. If we accept that the energy of interaction of the adsorbate molecules with the adsorbent is proportional to the C_6 constants, then the ratio of these constants coincides with that of the initial adsorption heats (1.4). If we take into account the difference in sizes of the methane and sulfur hexafluoride molecules, the ratio of the interaction energies would be even lower due to a larger size (*r*) of the SF_6 molecule.

The polarizability (α), magnetic susceptibility (χ), and size (*r*) of the SF_6 and CH_4 molecules and C atoms are presented below.

Molecule or atom	α /cm^3	$\chi \cdot 10^{-6}$ /cm^3 g-atom^{-1}	*r* /nm
SF_6	6.2	−6 [13]	0.251
CH_4	2.6	2.5 [14]	0.21
C	1.3	−6 [14]	0.077

The excess heats of adsorption of CH_4 on FAS carbon in the measured pressure region (Fig. 8) are almost independent of the extent of adsorption and coincide with the initial heat of adsorption of methane on CMS carbon. With further increase in CH_4 adsorption on CMS the excess heats of adsorption approach infinite values. The isosteric excess adsorption heats of sulfur hexafluoride on FAS and CMS, as can be seen in Fig. 8, increase monotonically with coverage up to an adsorption of 1 mmol g^{-1} due to the enhancement of adsorbate—adsorbate interaction.

The main expressions relating the temperature plot of the excess isosteric heat of adsorption to the partial molar (differential) heat capacity ($\partial C_a/\partial N_a$) of the adsorbed substance can be written as follows[2]:

$$\left(\frac{\partial q_{st}}{\partial T}\right)_\Gamma = \left(\frac{\partial C_a}{\partial N_a}\right)_T - (C_g)_P - \left(\frac{\partial h_g}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_\Gamma . \qquad (2)$$

Here $N_a = \Gamma$, $(C_g)_P$ is the heat capacity of the gas at constant pressure, and h_g is the molar enthalpy of the gas. The changes in the partial molar heat capacity $(\partial C_a/\partial N_a)_T$ of the adsorbate with coverage were calculated for the two systems SF_6—CMS and SF_6—FAS by Eq. (2). In the temperature interval in which the excess adsorption isosteres are nonlinear, the dependences of the isosteric adsorption heat on temperature and coverage were taken into account in the calculation of the differential heat capacity. The plots of the partial molar thermal capacity of sulfur hexafluoride adsorbed on FAS carbon *vs.* excess adsorption Γ for three temperatures, *viz.*, 298, 327, and 373 K, are shown in Fig. 9, *a*. For comparison, Fig. 9, *b* demonstrates the plots of the differential heat capacities of sulfur hexafluoride adsorbed on the FAS and CMS carbons against coverage $\theta = \Gamma/\Gamma_{max}$ at $T = 298$ K (Γ_{max} was determined from the Dubinin—Radushkevich (DR) equation).[15] At low coverages (θ = 0—0.4) the partial molar heat capacities of SF_6 adsorbed on the CMS and FAS carbons virtually coincide with the heat capacity of gaseous sulfur hexafluoride: $C_P{}^g = 0.099$ kJ K^{-1} mol^{-1}. This implies that over this range of coverages the adsorbent has no substantial effect on the thermophysical properties of the adsorbate.

As can be seen from the plot (see Fig. 9, *b*), the differential heat capacity of SF_6 adsorbed on FAS carbon takes infinite values at lower adsorption values than on CMS carbon (at θ = 0.5). This is related to the fact that the adsorption isosteres of SF_6 on FAS carbon

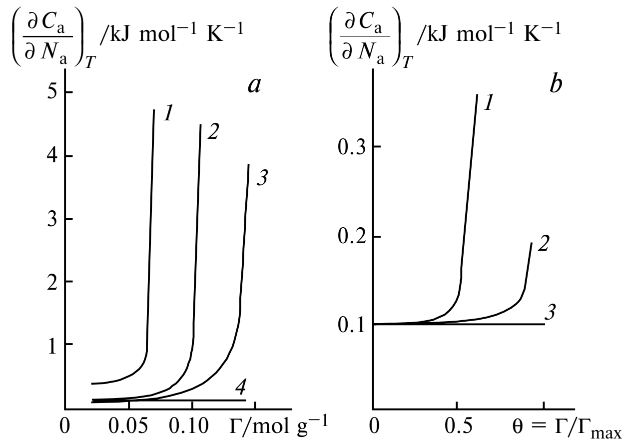

Fig. 9. Partial molar thermal capacity of SF_6 adsorbed on FAS and CMS: *a*, relation of the partial molar thermal capacity (*1—3*) at $T = 373$ (*1*), 327 (*2*), and 298 K (*3*) and $(C_g)_P$ (*4*) of SF_6 to the excess adsorption; *b*, plot of the partial molar thermal capacity (*1, 2*) and $(C_g)_P$ (*3*) of SF_6 adsorbed on FAS (*1*) and CMS (*2*) *vs.* coverage (θ) at $T = 298$ K.

show no linearity even at the lowest coverage ($\Gamma = 0.01$ mmol g^{-1}, see Fig. 6).

The calculated isosteric heats and differential heat capacities of excess adsorption coincide with the calorimetric data for gas adsorption only in the initial region of equilibrium pressures of adsorptives, whereas for vapor adsorption the calculated and experimental results coincide in a broader region.

Thermodynamic parameters of absolute adsorption. The difference of the absolute adsorption isosteres (see Figs. 1 and 2) from the excess adsorption isosteres (see Figs. 3—6) is that their linear regions expand toward higher temperatures and coverages. For the adsorption systems with microporous sorbents, the region of linearity of absolute adsorption isosteres is larger than that for the systems with sorbents containing a substantial volume of mesopores. For example, the linearity of isosteres is observed when CH_4 or SF_6 is adsorbed on a microporous sorbent at any experimental temperature and coverage (see Fig. 1). On the mesoporous FAS carbon, both adsorptives are adsorbed in different ways, and the calculation of the volumes of micropore volumes (W_0) with methane and benzene gives 0.20±0.03 and 0.17±0.02 cm^3 g^{-1}, respectively. These figures show that adsorption in mesopores makes an insignificant contribution to the value of total adsorption found experimentally. It should be expected for this system that the absolute adsorption isosteres are virtually linear as was observed for methane adsorption on CMS. For adsorption of sulfur hexafluoride on FAS carbon, only an insignificant fraction of the total volume of micropores (0.014 cm^3 g^{-1}) is involved in adsorption.[6] Since the main volume of micropores is inaccessible for the SF_6 molecules, the measurement of the volumes of micro- and mesopores for this adsorbate gives comparable results. A comparison of the absolute and excess adsorption isosteres (see Fig. 2) shows that the straight-line portion in the absolute adsorption isosteres of SF_6 on FAS carbon expands toward higher temperatures (from 313 to 343 K) and increased coverages (from 0.02 to 0.08 mmol g^{-1}).

Within the framework of statistical thermodynamics, the slope to the isostere can be expressed through the values that characterize the adsorbate—adsorbent and adsorbate—adsorbate interactions. Consider adsorbent consisting of similar cells. In the absence of interaction between the adsorbate molecules distributed through the cells, the adsorption isotherm *a* can be described by the equation[16]

$$a = (\partial \ln \Xi / \partial \ln \lambda)_T,$$

$$\Xi = 1 + Q + Q_1\lambda + Q_2\lambda^2 + \ldots + Q_n\lambda^n + \ldots,$$

$$\lambda = e^{\mu/(kT)}. \qquad (3)$$

Here Ξ is the great statistical sum, *n* is the number of adsorbed molecules in the adsorbent cell, λ is the absolute activity of the equilibrium gas, Q_1, Q_2, ... Q_n are the statistical sums of the states 1, 2, ... *n* of the molecules in the adsorbent cell, and μ is the chemical potential of the equilibrium gas. The porous carbon can be represented as a sorbent consisting of similar cells, which in the adsorption experiment behaves exactly as the porous carbon, *i.e.*, it obeys the same relation $F(a,\lambda,T) = 0$. Based on the known model,[16] the probability that *j* molecules are present in the adsorbent cell can be expressed by the equation

$$w_j(\lambda,T) = Q_j\lambda^j/\Xi. \qquad (4)$$

In the region of our measurements, w_j can be considered as a function of the index *j*, which is symmetrical relative to the most probable number of molecules j_0 at small deviations from j_0.[17] Assuming that j_0 coincides with the average number of molecules in the adsorbent cell j_{av}, *i.e.*, $j_0 = j_{av}$, and also from the condition of extreme for the function w_j, we obtain

$$(\partial w_j/\partial j)_{\lambda,T} = w_j(\partial \ln Q_j/\partial j + \ln\lambda) = 0. \qquad (5)$$

From where

$$(\partial \ln Q_j/\partial j)_{j0} = -\ln\lambda. \qquad (6)$$

It has previously[18] been shown that $\ln Q_j$ is sufficiently well described by the equation

$$\ln Q_j = (1/T)(a_1 j + a_{12} j^2 + a_{123} j^3) + Q_j^{\text{id}}, \qquad (7)$$

where Q_j^{id} is the statistical sum of the states *j* of the ideal gas molecules, and the coefficients a_1, a_{12}, and a_{123} are independent of *T* and λ.

Let us designate

$$(1/T)(a_1 j + a_{12} j^2 + a_{123} j^3) = \ln Q_j^*. \qquad (8)$$

It has been shown[16] that the derivative $[\partial \ln Q_j/\partial(1/T)]_\lambda$ is proportional to ε_j (the energy of *j* particles in the adsorbent cell) and, in the absence of adsorbate—adsorbate interaction, should be proportional to j, *i.e.*, in Eq. (8) the coefficients $a_{12} = a_{123} = 0$. Therefore, we may conclude that the a_1 coefficient characterizes the energy of the adsorbate—adsorbent interaction, and a_{12} and a_{123} differ from zero if the adsorbate—adsorbate interaction cannot be ignored. Taking into account the definition of volatility $\mu = \mu_0(T) + kT\ln f$ (here μ_0 is the chemical potential of this gas at the specified temperature T and volatility equal to unity), Eq. (6) can be written in the form

$$(\partial \ln Q_j/\partial j)_{j0} + \mu_0/kT = -\ln f. \qquad (9)$$

The volatility f is a function of the average number of particles (j_{av}) and T. By analogy to the previously published work[16]

$$[\partial \ln Q_j^{id}/\partial(1/T)] = \varepsilon_j^{id}/k = j\varepsilon^{id}/k. \qquad (10)$$

Then

$$-\ln f = \left(\frac{\partial \ln Q_j^*}{\partial j}\right)_{j_0} + \left(\frac{\partial \ln Q_j^{id}}{\partial j}\right)_{j_0} + \frac{\mu_0(f,T)}{kT} = $$
$$= \left(\frac{\partial \ln Q_j^*}{\partial j}\right)_{j_0} + \frac{1}{k}\int \varepsilon^{id} d(1/T) + \mu_0/(kT). \qquad (11)$$

The differentiation of both parts of Eq. (11) with respect to $1/T$ gives

$$\left[\frac{\partial \ln f}{\partial(1/T)}\right]_{j_0} = -\left[\frac{\partial^2 \ln Q_j^*}{\partial(1/T)\partial j}\right]_{j_0} + \frac{1}{k}(\varepsilon^{id} - h^{id}). \qquad (12)$$

Here ε^{id} is the energy of the ideal gas per particle, and h^{id} is the enthalpy of the ideal gas per particle,

$$\varepsilon^{id} - h^{id} = -kT. \qquad (13)$$

Then

$$\left[\frac{\partial \ln f}{\partial(1/T)}\right]_{j_0} = -\left[\frac{\partial^2 \ln Q_j^*}{\partial(1/T)\partial j}\right]_{j_0} - T =$$
$$= a_1 + 2a_{12}j_0\left[\frac{\partial j_0(f,T)}{\partial(1/T)}\right]_f + 3a_{123}j_0^2\left[\frac{\partial j_0(f,T)}{\partial(1/T)}\right]_f - T. \qquad (14)$$

The left part of Eq. (14) represents the slope of the adsorption isostere corresponding to j_0, and the right part includes several terms.

For strong adsorbate—adsorbent interaction, which is characteristic of adsorption on microporous adsorbents, a_1 is much higher than a_{12} and a_{123}. In this case, the slope of the adsorption isostere takes almost constant values. When in addition to the adsorbate—adsorbent interaction a contribution from other interactions is taken into account, the adsorption isostere would be essentially nonlinear. The curves of constant density of the gaseous adsorptive, isopycnes,[19] can serve as an example of such nonlinear isosteres.

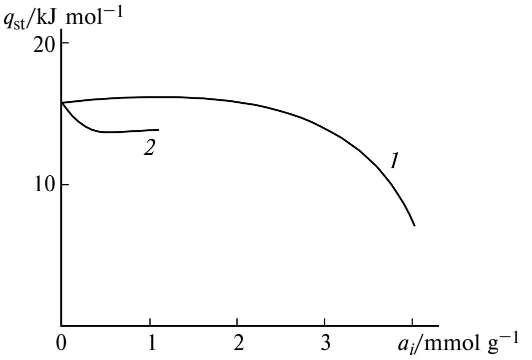

Fig. 10. Isosteric heats of absolute adsorption of CH_4 on CMS (*1*) and FAS (*2*).

Adsorption of SF_6 and CH_4 on the CMS carbon over the entire coverage region occurs mainly in micropores because the mesopore surface is insignificant. In this case, the energy of adsorbate—adsorbent interaction exceeds that of adsorbate—adsorbate interaction (Figs. 10 and 11). Since, the a_1 coefficient in Eq. (14) is much higher than the values of other terms, nearly linear form of the adsorption isosteres of sulfur hexafluoride and methane on CMS carbon would be expected as confirmed by the experimental data (see Fig. 1). Similar picture is observed for methane adsorption on FAS carbon when adsorption in micropores rather than in mesopores is prevailing. For SF_6 adsorption on the FAS carbon, the adsorption in mesopores is commensurable with that in micropores, and the energy of the adsorbate—adsorbent interaction in mesopores is lower than that for adsorption in micropores. This changes the ratio of the energies associated with adsorbate—adsorbent and adsorbate—adsorbate interactions. As a result, by

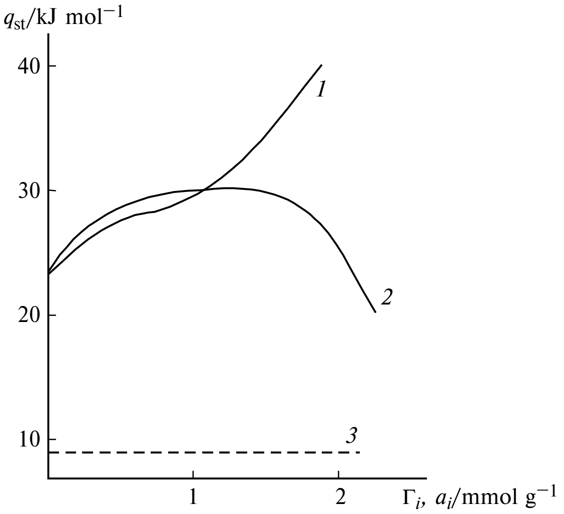

Fig. 11. Isosteric heats of excess (*1*) and absolute (*2*) adsorption of SF_6 on CMS carbon; *3*, condensation heat of SF_6.

description of SF_6 adsorption on FAS adsorbent, would be less influenced by a coefficient in Eq. (14). That is why the nonlinearity of the adsorption isosteres for this system would be expected as seen in Fig. 2.

The isosteric heats of absolute methane adsorption on the microporous carbon CMS (see Fig. 10, curve *1*) are virtually constant for coverages of up to 2.5 mmol g^{-1}. At higher coverages, the heat of adsorption decreases, and the behavior is most likely related to methane adsorption in larger pores followed by adsorption in mesopores. As expected, the isosteric heats of adsorption of methane on FAS carbon (see Fig. 10, curve *2*) remain unchanged over the range of coverages measured. They are close to the heat of adsorption of methane on CMS. The isosteric heats of absolute adsorption of SF_6 on the CMS carbon (see Fig. 11) behave similarly. Since the isosteres of absolute adsorption of SF_6 on FAS are nonlinear over the specific temperature interval, the change in the isosteric heats at different coverages is similar to the behavior of the isosteric heats of excess adsorption of SF_6 on CMS (see Fig. 11).

The main conclusions of the present study can be formulated as follows. For adsorption on pure microporous sorbents at high pressures, the isosteres of absolute adsorption are virtually linear over the wide range of temperatures and pressures, whereas the excess adsorption isosteres do not display a portion with a pronounced linearity. For microporous sorbents with the developed mesoporosity which show comparable adsorption values in micropores and mesopores, the isosteres of both excess and absolute adsorption are nonlinear. The nonlinearity of the adsorption isosteres on sorbents of this type is most likely due to a change in the average energy of adsorbate—adsorbent interactions that accompanies the transfer from adsorption in micropores to that in mesopores.

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