Features of sulfur hexafluoride adsorption on carbon adsorbents

A. A. Pribylov, I. A. Kalinnikova, and N. I. Regent*

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 952 5308. E-mail: pribylov@phyche.ac.ru

The isotherms describing excess adsorption of SF_6 and C_6H_6 on carbon adsorbents with different pore structures were measured at pressures of 0.001—2.4 and 0.0001—0.1 MPa, respectively, and temperatures of 298—408 K. A linear dependence of Henry's constant on temperature in the $\ln K$—$10^3/T$ coordinates was found for all the samples. The specific surface areas of the samples determined by the BET method from the SF_6 adsorption are lower than those derived from benzene adsorption. The most pronounced difference was found for the grafitized carbon black. When SF_6 was adsorbed on supermicroporous carbon AC-71 and on microporous carbons PAC and CMS, a hysteresis was found, which, unlike that on mesoporous carbon adsorbents, is observed in the initial region of the equilibrium pressures.

Key words: adsorption, carbon sorbents, sulfur hexafluoride, surface area, pore volume.

Sulfur hexafluoride is a good dielectric and a unique arc-quenching medium. An SF_6 admixture to freons decreases the boiling temperature of halones, and this property is used in refrigeration engineering. The triple point temperature is 226.36 K at a pressure of 2.3 atm.[1]

The processes of preparation and utilization of SF_6 are accompanied by the formation of various admixtures. Special gas-providing systems have been developed for the SF_6 utilization. The refining and drying of SF_6 are carried out by physicochemical methods including adsorption. The adsorption methods can be used for solving the problems of compressing and recovering SF_6 from the apparatus.

At the same time, few data on the SF_6 adsorption on adsorbents with various porosity are available in the literature. In this work, the equilibrium adsorption of SF_6 on a wide series of carbon adsorbents at pressures up to 2.2 MPa in the temperature range of 298—408 K is studied.

Experimental

The isotherms of the equilibrium adsorption of SF_6 on carbon sorbents in a wide range of pressures and temperatures were measured on a high-pressure volumetric-gravimetric adsorption setup developed by us.[2] The benzene adsorption on carbon sorbents was measured on another experimental setup that contains a bin balance with a 10 μg sensitivity and two manometers covering the whole range of measured pressures from 0.133 to $1.33 \cdot 10^5$ Pa. We used SF_6 (99.99%) and C_6H_6 (chemically pure grade) as the adsorptives. Grapitized carbon black, non-graphitized Vulkan carbon black, carbon fabric TU, microporous activated carbon CMS (Switzeland), as well as domestic microporous carbons SKT-6, PAC, activated carbon FAS with a developed mesoporosity, and supermicroporous carbon AC-71 were used as the adsorbents.

The equilibrium excess adsorption Γ was determined by the equation

$$\Gamma = (m - \rho_g V_{acc})/m_{ads}, \qquad (1)$$

where m is the amount of the adsorptive in the adsorber, ρ_g is the density of the equilibrium gas phase, V_{acc} is the accessible volume of the adsorber, and m_{ads} is the mass of the adsorbent in the adsorber. The accessible volume for CMS was estimated by the method developed by us[3] and that for the other adsorbents was determined as the volume of the ampoule without the volume of the weighted portion of the adsorbent. The experimental isotherms for the SF_6 excess adsorption on the AC, CMS, PAC, FAS, Vulkan carbon black, GTC carbon black, SKT-6 carbon black, and TU fabric adsorbents are presented in Figs. 1—4. Figure 5 shows the temperature dependences of the logarithm of Henry's constant for the SF_6 adsorption on the samples of the carbon adsorbents. Henry's constant for each adsorption system was found by approximating the measured equilibrim adsorption isotherms for SF_6 with a multiconstant equation, which is reduced to the Henry equation at $P \to 0$:

$$\Gamma = (K_1P + K_2P^2 + K_3P^3)/(1 + K_1P + K_2P^2 + K_3P^3), \qquad (2)$$

where K_1 is Henry's constant; Γ is the excess adsorption at the specified temperature and corresponding pressure P, and K_2 and K_3 are the constants of Eq. (2) determined by the nonlinear regression methods (*viz.*, the simplex and Newton methods).

Results and Discussion

The adsorption volumes (W) and surface areas (S) determined by different methods from the adsorption of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 839—844, April, 2003.

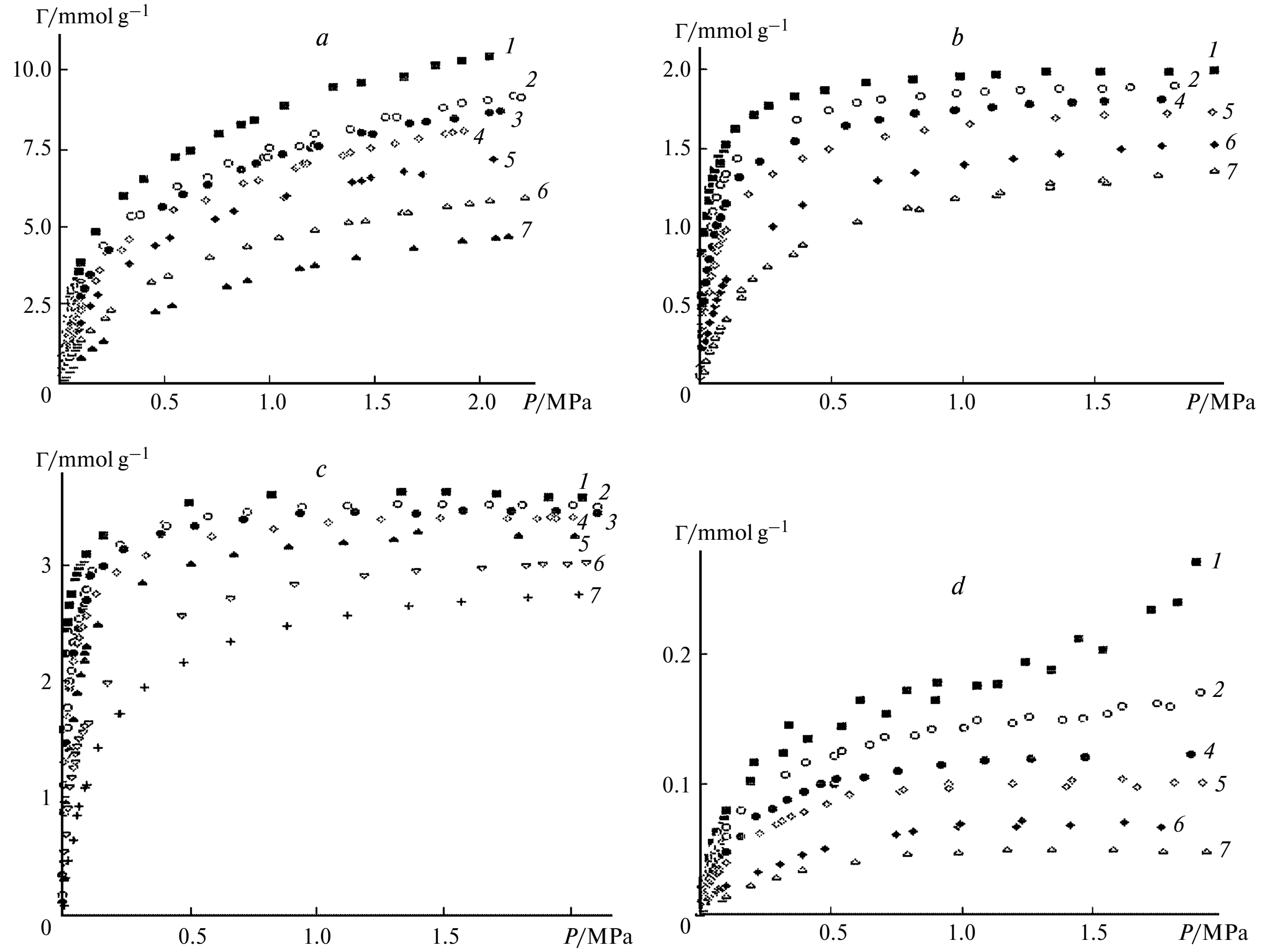

Fig. 1. Isotherms of excess adsorption of SF_6 on carbon AC-71 (*a*), CMS (*b*), PAC (*c*), and FAS (*d*) at different temperatures: 298 (*1*), 313 (*2*), 319 (*3*), 327 (*4*), 343 (*5*), 373 (*6*), and 408 K (*7*).

SF_6, CH_4, C_6H_6, and CO_2 on the adsorbents under study are presented in Table 1.

To calculate the *W* of adsorbents, the Dubinin—Radushkevich (DR) equation as well as the excess adsorption isotherm and the full content adsorption equation (EIAE) based on the Bakaev equation[4] were used. The Bakaev equation is based on assumption of independency that states that a molecule sorbed in any pore has no effect on molecules dwelling in other pores.

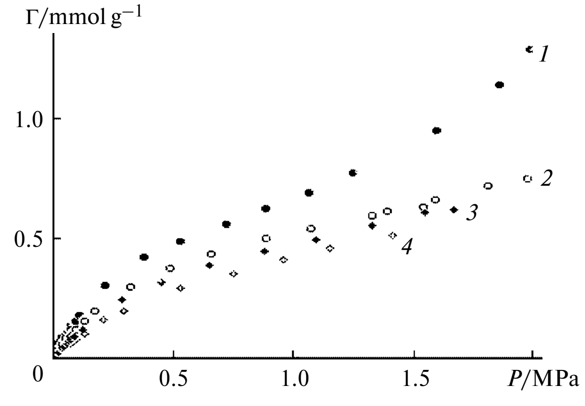

Fig. 2. Isotherms of excess adsorption of SF_6 on Vulkan carbon black at different temperatures: 298 (*1*), 319 (*2*), 327 (*3*), and 343 K (*4*).

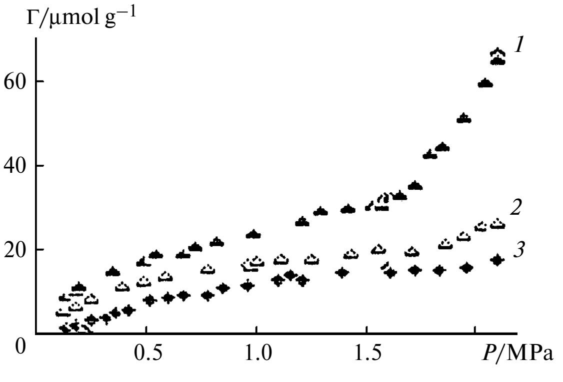

Fig. 3. Isotherms of excess adsorption of SF_6 on carbon black GTC at different temperatures: 298 (*1*), 327 (*2*), and 373 K (*3*).

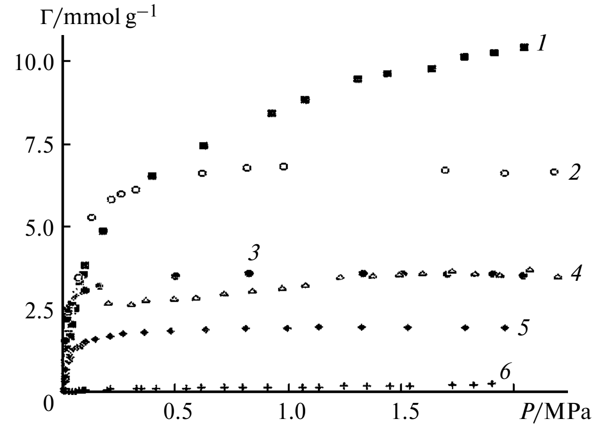

Fig. 4. Isotherms of excess adsorption of SF_6 at 298 K on various adsorbents: AC-71 (*1*), SKT (*2*), PAC (*3*), carbon fabric CF (*4*), CMS (*5*), and FAS (*6*).

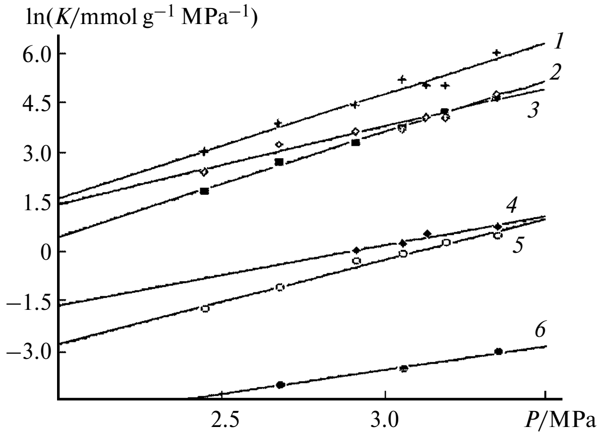

Fig. 5. Temperature dependence of Henry's constants (*K*) for SF_6 adsorption on various adsorbents: PAC (*1*), CMS (*2*), AC-71 (*3*), Vulkan carbon black (*4*), FAS (*5*), and carbon black GTC (*6*).

Table 1. Surface areas and pore volumes of adsorbents determined by various methods

Adsorbent	W_{mi}	W_{me}	S_{tot}	S_{me}	Method of measurement	Adsorptive	$S_{tot}(C_6H_6)$/$S_{tot}(SF_6)$
	cm^3 g^{-1}		m^2 g^{-1}				
Carbon CMS	—	—	—	28	CP	C_6H_6	2.4
	—	—	710	—	IH	C_6H_6	
	—	—	708	—	2ad	CH_4, SF_6	
	—	—	294	—	BET	SF_6	
	0.25	—	—	—	DR	C_6H_6	
	0.194	—	—	—	DR	SF_6	
	0.24	—	—	—	EIAE	CH_4	
Carbon FAS	0.163	—	690	86	CP	C_6H_6	8.7*
	—	—	—	78	γ′	C_6H_6	
	—	—	22	—	BET	SF_6	
	0.176	—	—	—	DR	C_6H_6	
	0.014	—	—	—	DR	SF_6	
	—	0.3	—	—	Technical sertificate		
	—	0.04	—	—	Halsey eq.	SF_6	
Carbon AC-71	—	—	1870	—	CP	C_6H_6	2.1
	—	—	2000	—	BET	N_2	
	—	—	932	—	BET	SF_6	
	1.01	—	—	—	DR	N_2	
	0.73	—	—	—	DR	SF_6	
Carbon SKT-12	—	—	1250	—	BET	C_6H_6	2.2
	—	—	565	—	BET	SF_6	
	0.65	—	—	—	DR	SF_6	
Carbon PAC	—	—	1990	—	2ad	CO_2, SF_6	4.38
	—	—	2000	—	BET	C_6H_6	
	—	—	454	—	BET	SF_6	
	0.52	—	—	—	DR	CO_2	
	0.311	—	—	—	DR	SF_6	
GTC carbon black	—	—	29.0	—	BET	C_6H_6	8.8
	—	—	3.33	—	BET	SF_6	
Vulkan carbon black	—	—	106	—	BET	C_6H_6	1.4
	—	—	72	—	BET	SF_6	

* $S_{me}(C_6H_6)/S_{me}(SF_6)$.

This principle holds for the carbon sorbents. To calculate the value of W for the mesoporous carbon sorbents, we calculated the thickness of the adsorption layer by the Halsey equation[5] and the total surface area (S_{tot}) of the adsorbent.[6]

To calculate the total surface area (S_{tot}), we used the following methods: the BET equation; the comparison plot (CP) for adsorption of a given substance on carbon black and on the sample under study; the γ-method (γ); the method based on the immersion heats (IH); the method based on the difference in the effective radii r_a and r_b of the molecules of two adsorptives (2ad) and in the adsorption volumes W determined with these two adsorptives (see Table 1):

$$S = (W_a - W_b)/(r_b - r_a). \quad (3)$$

For example, the $W_a(SF_6)$ and $W_b(CH_4)$ values (see Table 1), $r_a(SF_6)$ = 0.275 nm and $r_b(CH_4)$ = 0.21 nm were used for carbon CMS, whereas the $W_a(SF_6)$ and $W_b(CO_2)$ values were used for PAC. The $r_b(CO_2)$ = 0.17 nm[7] value was chosen for the case when the molecule is attached by two O atoms to the sorbent surface, and this value has been confirmed experimentally[2] for the N_2—NaA system.

The W values for the PAC and CMS microporous sorbents coincide with their pore volumes. These volumes also coincide in the case of the adsorption of the adsorptive with large molecules (SF_6) on supermicroporous AC-71. The pore volume of the adsorbent depends on the effective size of the adsorptive molecule, and one of the methods for estimation of the surface area used in this work is based on this dependence. The molecular-sieve effect is clearly pronounced in SF_6 adsorption on carbon FAS, which contains a large fraction of mesopores along with micropores. In this case, adsorption occurs only in mesopores whereas micropores remain inaccessible to the adsorptive.

The mesopore surface area in carbon FAS was determined by the CP method for two adsorptives, C_6H_6 and SF_6, at T = 298 K, and Vulkan carbon black was used as the second adsorbent.

The experimental isotherms of the SF_6 excess adsorption on carbon sorbents (see Figs. 1—4) show the effect of the sorbent pore structure on the adosrption of this substance. For instance, the isotherms of the SF_6 adsorption on the CMS and PAC microporous carbons (see Fig. 1, *b*, *c*) are characterized by a larger slope in the initial pressure range than the adsorption isotherms of the other adsorbents studied and higher values of Henry's constants (K), respectively. This is confirmed quantitatively by the linear temperature dependences of Henry's constants (see Fig. 5), which allow calculation of the isosteric heat of adsorption by the equation[8]

$$\ln K = K_0 + q_{st}^0/T. \quad (4)$$

Table 2. Constants of Eq. (4)

Adsorbent	q_{st}^0 /kJ mol^{-1}	$-K_0$ /kJ K^{-1} mol^{-1}
PAC	25.8	4.6
CMS	25.8	5.7
FAS	21	7.7
AC-71	19	3.1
GTC carbon black	11.6	7.9
Vulkan carbon black	14.9	5.1

Here $K_0 = \Delta S_1/R$, ΔS_1 is the difference between the differential molar entropy of the adsorptive and the mean molar entropy of the gas and q_{st}^0 is the initial isosteric heat of adsorption. The initial heat of adsorption, which is related to the energy of the adsorptive—adsorbent interaction, mainly determines the slope of the isotherms in the initial sections. Therefore, one should expect that q_{st}^0 will be larger on the microporous sorbents PAC and CMS than on the supermicroporous adsorbent AC-71 and substantially larger than on the carbon blacks (Table 2). However, the initial isosteric heats of adsorption are not related to the adsorption values on these adsorbents. For example, the supermicroporous carbon AC-71 has the highest adsorption capacity to SF_6 and its Henry's constant is less than that for the microporous carbons (see Fig. 4).

The K_0 value that can be found from the K temperature dependence (see Fig. 5) is associated with the adsorbtive entropy, which includes the thermal and configuration components. The latter should increase with an increase in both the adsorption volume and surface area of the adsorbent. The data in Tables 1, 2 and Fig. 5 illustrate the above suggestion. The temperature dependences of K for the PAC and CMS microporous carbons (see Fig. 5, straight lines *1* and *2*) run parallel, *i.e.*, the q_{st}^0 values are close (see Table 2) and the slope of these plots is larger than that for carbons FAS and AC-71, and two carbon blacks. At the same time, the constants K_0 obtained from the linear dependences of Henry's constants for the carbon PAC are greater than those for CMS, FAS, and the Vulkan and GTC carbon blacks (see Table 2), being in good agreement with the W and S values for these adsorbents (see Table 1). The initial isosteric heat of adsorption for carbon AC-71 (19 kJ mol^{-1}) is lower than those for all the other carbons (see Table 2) but this carbon have the highest adsorption capacity and adsorption volume to SF_6 (see Fig. 3, Table 1) as well as the K_0 value (see Table 2). The monoporous nature of carbon AC-71 is confirmed by the constant heats of adsorption up to the coverage of ~8 mmol g^{-1} (Fig. 6). The isotherm of the SF_6 adsorption at 298 K in the wide range of pressures is linear in the coordinates of the DR equation with the exponent n = 2 (Fig. 7). As mentioned above, the majority of

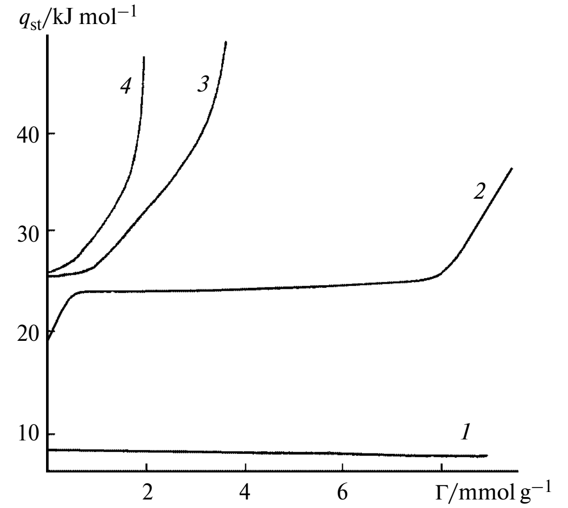

Fig. 6. Heat of condensation of SF_6 (*1*) and isosteric heats of excess adsorption of SF_6 on various adsorbents: AC-71 (*2*), PAC (*3*), and CMS (*4*).

micropores in carbon FAS are inaccessible to the SF_6 molecules. It follows from both the analysis of the adsorption data for C_6H_6, CH_4 ($\Gamma_{max} \approx 2$ mmol g^{-1}),[6] and SF_6 ($\Gamma_{max} \approx 0.2$ mmol g^{-1}) and the calculated W values for these adsorptives (see Table 1). It can be seen in Table 1 that the micropore volume (W_{mi}) for carbon FAC calculated from the C_6H_6 adsorption by the DR method is close to the adsorption volume determined by the CP method with C_6H_6. Hence, a mean pore volume determined with these two methods is $\langle W \rangle = 0.17 \pm 0.03$ cm^3 g^{-1}. When SF_6 is adsorbed, the micropore volume of this carbon calculated by the DR method at temperatures of 298 and 313 K is equal only to 0.014 cm^3 g^{-1} and the SF_6 adsorption in these micropores is comparable with that in mesopores. Because of small micropore volume, carbon FAC has the lowest adsorption capacity with respect to SF_6 (see Fig. 4) and low K_0 value (see Table 2). Since the initial adsorption of the substance occurs on the energetically strongest sites, *i.e.*, in the micropores, then the initial isosteric heat of SF_6 adsorption on carbon FAC, which is equal to 21 kJ mol^{-1}, is close to the $q_{st}{}^0$ value for the CMS and PAC carbons.

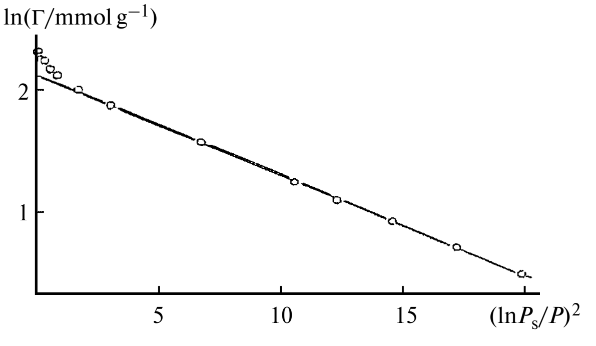

Fig. 7. Isotherm of excess adsorption of SF_6 on carbon AC-71 at temperature 298 K in the coordinates of the Dubinin—Radushkevich equation.

Compared to the initial heat of adsorption obtained from K, the heats of the SF_6 adsorption (see Fig. 6) increase monotonically with the coverage on the CMS and PAC carbons (curves *3* and *4*) This increase is due to the adsorptive—adsorptive interaction. With further coverage the values of heats tend to infinity. However, this does not reflect the real energetics of adsorption. As has been shown earlier,[9] the isosteric heats of adsorption determined from isosteres at the constant excess adsorption approach to infinity at $\Gamma \approx \Gamma_{max}$. The explanation is that the isotherms of excess adsorption measured in a wide range of pressures pass through a maximum or approach it. As a result, the isosteres of excess adsorption are curved and pass through the $\pi/2$ angle or approach it. Hence, the trend of the isosteric heats of adsorption to infinity is not a consequence of the real energy characteristics of the adsorption process.

The surface areas of all the carbon adsorbents found from the SF_6 adsorption by the BET method are lower than those determined with other adsorptives or by other independent methods (see Table 1). The most pronounced difference is seen when adsorption behavior of SF_6 and C_6H_6 on the energetically uniform GTC surface is compared.

There is a restriction in the application of the BET method for adsorption systems,[10] namely, the model requires that the C value in the equation

$$\frac{P/P_s}{a(1-P/P_s)} = \frac{1}{a_m C} + \frac{C-1}{a_m C} P/P_s, \qquad (5)$$

which is related to the molar heat of adsorption, shall exceed two.

In the case of the SF_6 adsorption on the carbon sorbents under study, the C value is greater than 10. We performed measurements in the temperature range 197—531 K in which the proposed[11] area for the SF_6 molecule is 0.264—0.267 nm^2. Nevertheless, the results of calculations show that the BET method is inapplicable for estimation of the surface areas of carbon adsorbents from the SF_6 adsorption at temperatures 298—313 K. Although the BET equation (5) does not contain the temperature term, temperature indirectly affects the uptake because the P_s value enters the equation. It seems that the isotherms of the SF_6 adsorption on the GTC and Vulkan carbon blacks were measured at insufficiently low temperatures, since this temperature range is close to the critical temperature in the case of SF_6 and to the boiling point in the case of C_6H_6. Therefore, the SF_6 molecule occupies only strong adsorption sites.

The value of SF_6 adsorption (Γ) on GTC and the surface area S_{tot} calculated by the BET method proved to be ~8.8 times lower than those obtained with C_6H_6 (see

Table 1). When these values (S_{tot}) obtained with two adsorptives are compared with similar values derived from adsorption on Vulkan carbon black that has significantly more "active" sites than GTC, the ratio between S_{tot} determined by the BET method with the use of C_6H_6 and S_{tot} determined with SF_6 is only 1.4 and this value is much lower than that for GTC. This means that the BET method with the use of SF_6 detects only a fraction of the surface occupied by the molecules adsorbed on the active sites rather than the total surface area of the adsorbent corresponding to a complete monolayer. The energy of interaction of the SF_6 molecules on these sites can be estimated from the slopes of the linear temperature dependencies of $\ln K_g$ for the graphitized and Vulkan carbon blacks (see Fig. 5). These values proved to be close to each other, *i.e.*, the initial heats of SF_6 adsorption on these carbon blacks are nearly equal. Thus, introducing SF_6 adsorption on these carbon blacks and using BET calculations one can determine the fraction of more "active" sites rather than the amount of sites corresponding to a complete monolayer of the molecules (based on 1 g of adsorbent). This value for the Vulkan carbon black is $27.2 \cdot 10^{19}$, whereas for graphitized carbon black it is $1.26 \cdot 10^{19}$, *i.e.*, the first is nearly 20 times higher (the number of the "active" sites was determined from the monolayer capacity by the BET method).

When SF_6 is adsorbed on the supermicroporous carbon AC-71 (Fig. 8) and on the microporous PAC and CMS carbon sorbents, hysteresis is observed. In contrast to hysteresis usually found for mesoporous adsorbents, the loop appears in the initial range of the equilibrium pressures at temperatures, which are lower and higher than critical temperature (T_{cr} = 318.69 K). The initial heats of the SF_6 adsorption were estimated from the $\ln K$ temperature dependence (Fig. 9) for the adsorption and desorption isotherms. The initial heats of adsorption for the adsorption and desorption branches of the isotherms differ by the $\Delta q = q_{des} - q_{ads}$ value. This difference was ~4 kJ mol^{-1} for carbon PAC and ~3 kJ mol^{-1} for carbon AC-71.

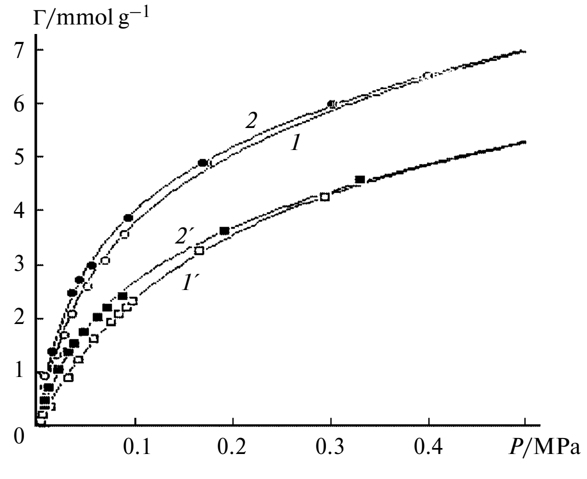

Fig. 8. Adsorption (*1*, *1′*) and desorption (*2*, *2′*) isotherms of excess adsorption of SF_6 on carbon AC-71 at 298 (*1*, *2*) and 327 K (*1′*, *2′*).

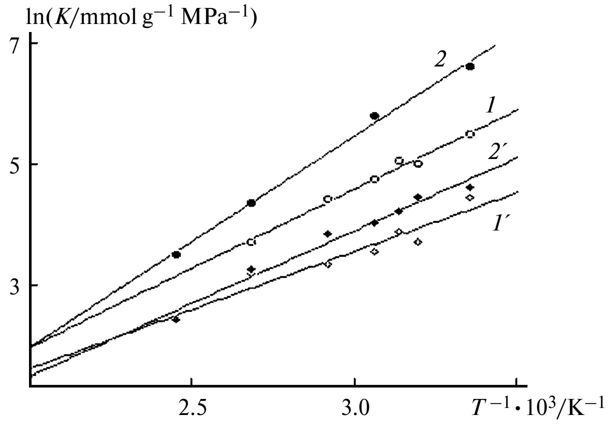

Fig. 9. Temperature dependence of Henry's constants (K) obtained from adsorption isotherms 1(*1*, *1′*) and desorption (*2*, *2′*) isotherms for SF_6 on PAC (*1*, *2*) and AC-71 (*1′*, *2′*).

The adsorption hysteresis at temperatures 293.1, 313.1, 319.3, and 323.1 K has been found[12] for the equilibrium SF_6 adsorption on the graphitized adsorbent GRAFOAM ($S = 26.2 \pm 1.3$ m^2 g^1). The desorption isotherms of SF_6 lie far above than the adsorption isotherms over the whole range of pressures. Beyond the critical temperature, deviation between the adsorption and desorption branches is observed in the vicinity of the highest adsorption values. The hysteresis effect decreases upon the repeated cycles of the adsorption—desorption measurements. The authors of work[12] ascribed the appearance of hysteresis to deformation of carbon aggregates caused by nonuniform compression of the material during adsorption. As a result, gas penetrates the slits between graphite crystallites, which were earlier inaccessible.

The main conclusions from this study can be formulated as follows. When SF_6 is adsorbed on microporous carbons, the molecular-sieve effect arises due to a great kinetic diameter of the SF_6 molecule (0.513 nm) compared to a pore size. The surface areas found by the BET method from the SF_6 adsorption and, for instance, from the C_6H_6 adsorption, differ markedly from each other. This difference is especially great for the GTC and Vulkan carbon blacks because SF_6 adsorption indicates only a fraction of the surface occupied by the molecules adsorbed on the strong sites rather than the total surface area corresponding to a complete monolyer. When SF_6 is adsorbed on carbons CMS, PAC, and AC-71, the hysteresis is observed. In contrast to conventional hysteresis it arises in the initial range of equilibrium pressures at temperatures, which are lower and higher than the critical temperature, the phenomenon apparently associated with the adsorbent deformation upon adsorption.

References

1. A. A. Opalovskii and E. U. Lobnov, *Usp. Khim.,* 1975, **44**, 193 [*Russ. Chem. Rev.*, 1975, **44** (Engl. Transl.)].
2. A. A. Pribylov, *Izv. Akad. Nauk, Ser. Khim.,* 1996, 574 [*Russ. Chem. Bull.*, 1996, **45**, 539 (Engl. Transl.)].
3. A. A. Pribylov and G. F. Stoekli, *Zh. Fiz. Khim.,* 1998, **72**, 306 [*Russ. J. Phys. Chem.*, 1998, **72**, No. 2 (Engl. Transl.)].
4. V. A. Bakaev, *Dokl. Akad. Nauk SSSR,* 1966, **167**, 369 [*Dokl. Chem.*, 1996 (Engl. Transl.)].
5. G. D. Halsey, *J. Chem. Phys.*, 1948, **16**, 931.
6. A. A. Pribylov, I. A. Kalinnikova, S. M. Kalashnikov, and G. F. Stoekli, *Izv. Akad. Nauk, Ser. Khim.,* 2000, 688 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 692].
7. D. W. Breck, *Zeolite Molecular Sieves,* Wiley-Interscience, New York—London—Sydney—Toronto, 1974.
8. A. A. Lopatkin, *Teoreticheskie osnovy fizicheskoi adsorbtsii* [*Theoretical Bases for Physical Adsorption*], Izd-vo MGU, Moscow, 1983, 150 pp.
9. A. A. Pribylov, I. A. Kalinnikova, L. G. Shekhovtsova, and S. M. Kalashnikov, *Izv. Akad. Nauk, Ser. Khim.,* 2000, 2026 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1993].
10. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London—New York, 1967, 306 pp.
11. A. L. McClellan and H. F. Harnsberger, *J. Colloid Interface Sci.*, 1967, **23**, 577.
12. R. Susmann, K. Neumann, and G. H. Findenegg, *Characterization of Porous Solids*, Elsevier, Amsterdam, 1988, 203.

Received May 15, 2002;
in revised form December 2, 2002