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Adsorption of Methane on Microporous Carbonaceous Adsorbent at High Pressures and Temperatures

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Abstract—The adsorption and desorption isotherms for methane on microporous carbonaceous adsorbent were measured at pressures of 0.5 to 160 MPa and temperatures of 313, 373, and 408 K. The adsorption volume W of CMS microporous carbonaceous adsorbent was determined based on the experimental values of the Gibbs adsorption and the isotherm equation with the use of the method elaborated by us. The obtained value of W is close to that derived from Dubinin's theory of volume filling of micropores. In this case, the isosteric adsorption heats are higher by the factor ~1.5 than those for the CH_4–NaX system.

INTRODUCTION

Most studies of the adsorption of various substances on carbonaceous adsorbents have been carried out at low pressures of adsorptives. Under these conditions, the Gibbs adsorption Γ virtually coincides with the absolute adsorption a. In this range of pressures p of adsorptives, the isosteric heat of the Gibbs adsorption q_{st}^{Γ} is given by the equation [1]

$$q_{st}^{\Gamma} = -ZR(d\ln p/dT)_{\Gamma} \qquad (1)$$

(Z is the coefficient of compressibility of adsorptive, R is the gas constant) and is always finite.

At high adsorptive pressure, the Gibbs adsorption isotherms $\Gamma = \Gamma(p)$ differ qualitatively from the absolute adsorption isotherms $a = a(p)$. The $a(p)$ isotherms are growing functions of p over the entire pressure range up to the maximum filling; in contrast, the Gibbs adsorption isotherms $\Gamma(p)$ initially increase, reach a maximum, and then fall to zero [2–4]. The Gibbs adsorption isosteres in the region of the maximum adsorption are nonlinear functions; at the point of the isotherm maximum, the q_{st}^{Γ} value tends to infinity, which is physically unreasonable.

In order to eliminate this contradiction, it is necessary to recalculate the experimental values of Γ into a. To do this, it is necessary to know the limiting volume of adsorption W, which may not coincide with the geometric volume of the adsorbent pores. Note that spectroscopic and calorimetric measurements and sorption-based technologies deal with the absolute adsorption, because the signal from all the molecules in the adsorption space is detected.

In contrast to crystalline porous solids (zeolites), the carbonaceous adsorbents (activated carbon) have pores varying in size; therefore, the determination of the adsorption volume of a carbonaceous adsorbent is a complicated problem. In addition, the adsorption of gases on activated carbon at high pressures and elevated temperatures is poorly understood.

The aim of this study is to investigate the behavior at high adsorptive pressures of the methane–CMS activated carbon system.

EXPERIMENTAL

In this work, we used CMS granulated microporous carbonaceous adsorbent (Switzerland). CMS porous adsorbent is characterized by the following structural and energetic parameters, which were derived from the theory of volume filling of micropores (TVFM) [5, 6]: the characteristic energy of adsorption $E_0 = 26.19$ kJ/mol, micropore volume $W = 0.252$ cm^3/g, specific surface area of mesopores $s_{me} = 28.0$ m^2/g, and average pore radius $L = 0.8$ nm. The weight of the sample m_{ad} evacuated at 623 K was 1.3514 g. Methane of pure grade (99.8 vol % CH_4 and 0.2 vol % N_2) was used as an adsorptive; before use it was passed through a zeolite trap cooled by liquid nitrogen to remove moisture, carbon dioxide, and heavy hydrocarbons.

The experiments were carried out in a volumetric–gravimetric adsorption high-pressure setup we developed for this purpose. A metallic autoclave (3.001 cm^3 in volume) packed with the adsorbent was suspended on an arm of a VLR-200 analytical balance; methane was supplied to the adsorbent through a thin metallic spiral-shaped capillary. The absolute sensitivity of the measuring system was 5×10^{-4} g. A more detailed description of the experimental procedure is given in [7]. (The installation used in this study is distinguished only by the presence of a gravimetric manometer of our construction connected in parallel to a Bourdon pressure gage. This manometer was similar to the volumetric–

gravimetric setup in design and accuracy.) The gravimetric manometer was kept at 300 ± 0.1 K. Due to the relatively large volume of the autoclave of the gravimetric manometer (13.157 cm^3), the methane density at the stage of adsorption equilibrium, ρ_Γ, was measured to an accuracy of 1% at low pressures; at higher pressures, the accuracy was higher. The pressure of methane was calculated from the measured ρ_Γ and T values by the multiconstant equation of state of methane $F = (p, \rho, T)$ [8]. The error in the methane pressure determined by this equation was below 1% over the entire pressure range covered.

RESULTS AND DISCUSSION

In order to determine the Γ value, it is necessary to substrate, from the total weight of gas in the autoclave filled with the adsorbent, the weight m_a of gas in the accessible volume V_a ($m_a = V_a\rho_\Gamma$)

$$V_a = V_f + W. \qquad (2)$$

Here, ρ_Γ is the density of the equilibrium gas phase, V_f is the fraction of the autoclave volume free from the adsorbent, and W is the limiting volume of adsorption (for a microporous carbonaceous adsorbent, this is the volume of the micropores plus a volume in mesopores that is equal to the product of the surface area s_{me} of mesopores and the width of the adsorption space). Inasmuch as the density of the equilibrium gas over the pressure range covered is high, and $V_f \gg W$ for the activated carbon, even a small error in the V_a value can lead to large uncertainty in the Gibbs adsorption calculated by the equation

$$\Gamma = (m - \rho_\Gamma V_a)/m_{ad}, \qquad (3)$$

where m is the weight of adsorptive in the autoclave packed with adsorbent. Therefore, the calibration procedure should be performed thoroughly. Normally, helium is used to calibrate the adsorption apparatus because it is not adsorbed at room temperature and low pressures. However, the accessible volume V_a depends on the apparent diameter of the calibration gas molecule [9]. Because of this, the difference in the sizes of He and an adsorptive molecule may lead to the overestimation of the V_a value calculated by equation (3); this, in turn, yields an underestimated value of Γ. In [2–4], it is shown that the calibration of the adsorption cell can be made with the adsorptive under investigation. One advantage of such a procedure is that it becomes a part of adsorption isotherm measurements.

The principle of this procedure is as follows. At a specific pressure, a gas density ρ_Γ is achieved that is equal to the average density ρ_a of the adsorbate phase in the volume of adsorption W

$$m/\rho_\Gamma = m_f/\rho_\Gamma + m_a/\rho_\Gamma = V_f + W\rho_a/\rho_\Gamma. \qquad (4)$$

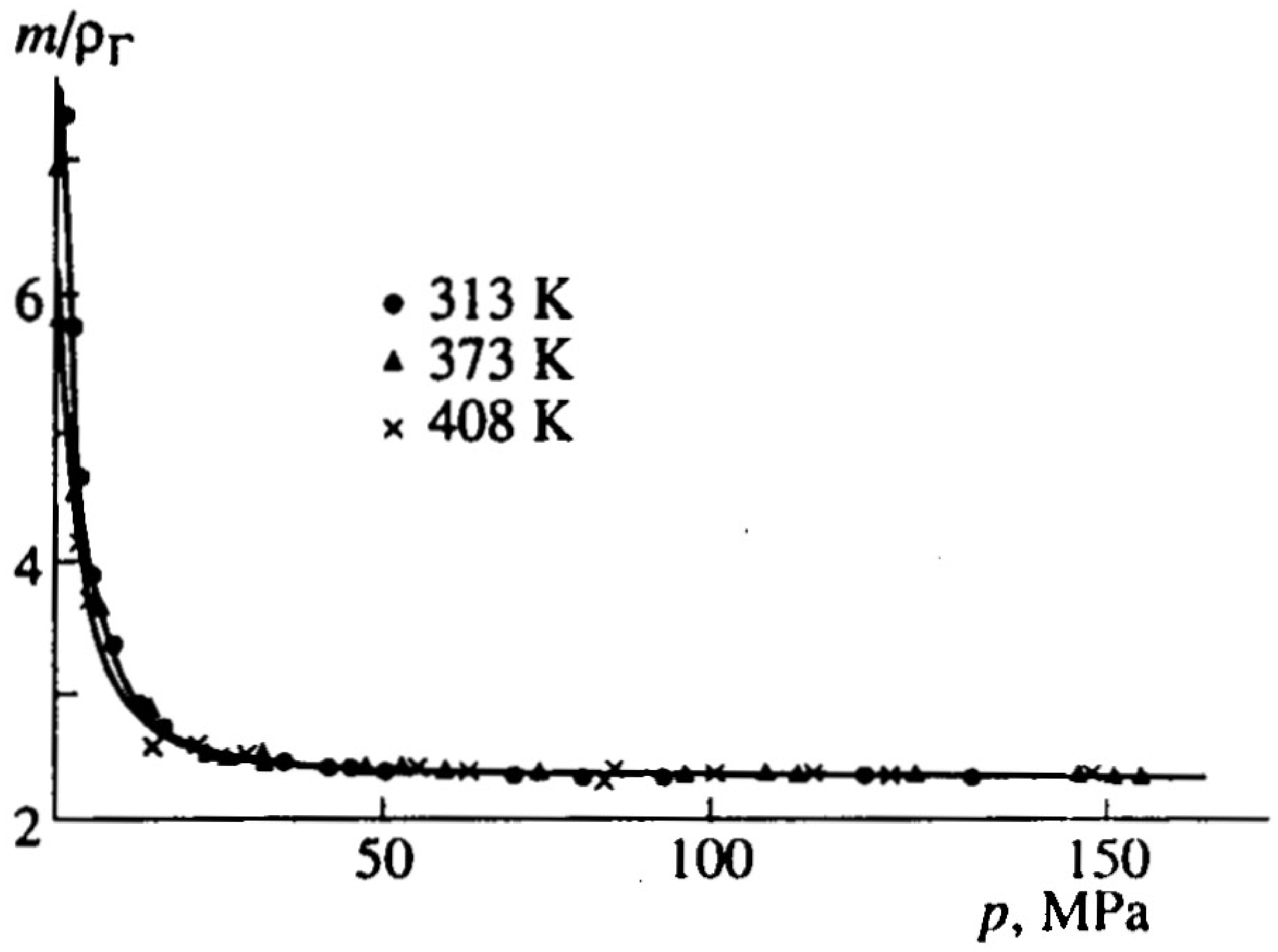

Fig. 1. Calibration curves for determining the accessible volume V_a.

Here, m_f is the weight of gas occupying the volume V_f in the autoclave packed with an adsorbent, and m_a is the weight of gas in the volume of adsorption. Then there must be a horizontal segment in the $m/\rho_\Gamma = V$ vs. p plot with $V = V_a$ [equation (2)]. Figure 1 displays the results of calibration for the CH$_4$–CMS system at 313, 373, and 408 K. For the adsorption and desorption branches of the curve measured at 313 K, $V_a = 2.331 \pm 0.003$ and 2.342 ± 0.003 cm^3, respectively. The fact that the latter value is somewhat higher suggests that the volume of pores changes during adsorption. Measuring V_a at 373 and 408 K in subsequent experiments, we found that the values of V_a for the adsorption and desorption branches are almost the same, 2.346 ± 0.008 cm^3, within the limits of the experimental error. This value of V_a was used to construct the adsorption isotherms Γ for the three temperatures. Figure 2 shows these adsorption isotherms. The V_a values were determined at pressures of 100 to 160 MPa; the deviations of the values of V_a from the mean value were random. The correctness of the determined value of V_a can be checked in the following manner. Dividing the weight of the adsorbent by the difference between the autoclave volume (3.001 cm^3) and V_a, we determine the density of CMS microporous carbonaceous adsorbent to be 2.063 ± 0.019 g/cm^3, a value close to the density of graphite (2.26 g/cm^3) [10] and graphitized carbon blacks (2.053 ± 2.178 [11]). In [12], the density of four types of carbonaceous adsorbents measured by making use of the He calibration was found to be 2.04–2.20 g/cm^3.

In an effort to describe the Gibbs adsorption Γ analytically as a function of the density of the equilibrium gas phase (Fig. 2), we used an expression similar to the Dubinin–Radushkevich equation [13]

$$\Gamma(\rho) = \Gamma_m \exp(-RT/E)^2 \left|\ln\frac{\rho_m(\rho_b - \rho)}{\rho(\rho_b - \rho_m)}\right|^2. \qquad (5)$$

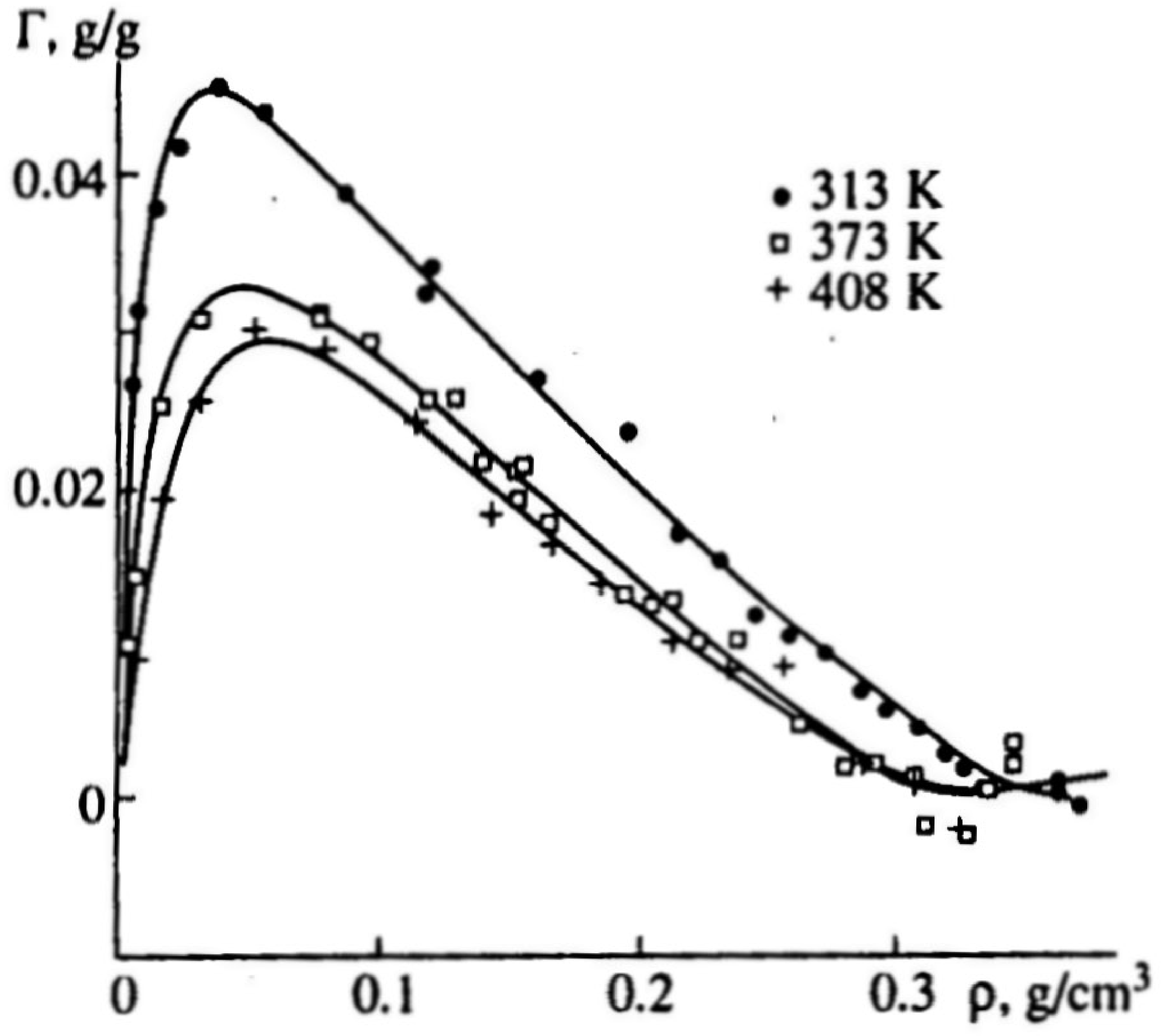

Fig. 2. Excess adsorption isotherms of CH_4 on CMS activated carbon.

Here, ρ_m and Γ_m are the coordinates of the isotherm peak, ρ_b is a gas density at which the Gibbs adsorption is zero, and E is the energetic parameter which is equal to 6871 kJ/mol for the $T = 313$ K isotherm. The temperature dependences of the parameters of equation (5) are adequately described by the relations [4]:

$$\begin{aligned} \Gamma_m(T) &= \Gamma_m(T_0)\exp[-\alpha(T-T_0)], \\ \rho(T)_m &= \rho_m(T_0)\exp\left[\beta\frac{T-T_0}{TT_0}\right], \\ \rho_b(T) &= \rho_b(T_0)\exp\left[\gamma\frac{T-T_0}{TT_0}\right], \\ E(T) &= E(T_0)\exp\left[\kappa\frac{T-T_0}{TT_0}\right], \end{aligned} \qquad (6)$$

where α, β, γ, and κ are the corresponding temperature coefficients, and T_0 is the reference temperature (in our case, 313 K).

To construct the adsorption isotherm $a = a(p)$, it is necessary to add the product of the current density ρ_i of the equilibrium gas and the volume of adsorption W to each ordinate of the experimental excess adsorption Γ.

The volume of adsorption W of CMS adsorbent was determined by two methods, which are based on the theory of volume filling of micropores (TVFM) and on the approach developed by us in [14]. The latter method is suitable not only for microporous carbonaceous adsorbents, but also for adsorbents of an arbitrary porous structure. The method is based on the universal relation existing between the absolute a and Gibbs Γ adsorptions

$$a(p, T) - \rho(p, T)W = \Gamma(p, T). \qquad (7)$$

To use this equation one should obtain the experimental adsorption isotherm $\Gamma = \Gamma(p)$, in a wide pressure range, and the equation of the adsorption isotherm $a = a(p)$ with indeterminate coefficients (derived from the statistic thermodynamics; see, for example, [15]). In this method, the parameters of the equation $a = a(p)$ and the W value at each point of the isotherm are adjusted so as to obtain agreement between the calculated Γ^{calc} and measured Γ^{expt} Gibbs adsorption; i.e., the functional

$$\Phi = N^{-1}\sum[(\Gamma_i^{expt} - \Gamma_i^{calc})/\Delta\Gamma_i^{expt}]^2 = \min \qquad (8)$$

is minimized. Here, $\Delta\Gamma^{expt}$ is the experimental error in Γ determination.

The limiting volume of adsorption for CMS microporous carbonaceous adsorbent is $W = 0.246 \pm 0.015$ cm³/g at the three temperatures used. This value agrees well with $W = 0.252$ cm³/g, a value obtained based on the TVFM approach. The limiting volumes of adsorption determined from the adsorption and desorption branches of the $T = 313$ K isotherm curve by the method of [14] are $W_{ad} = 0.239 \pm 0.011$ and $W_{des} = 0.253 \pm 0.008$ cm³/g, respectively. The difference between these quantities, $\Delta W = 0.014$ cm³/g, agrees closely with the results obtained for the same isotherms during calibration of the autoclave volume V_a packed with the adsorbent: $V_a^{ad} = 2.331 \pm 0.003$ and $V_a^{des} = 2.342 \pm 0.003$ cm³, with $\Delta V_a = 0.011$ cm³/g; this demonstrates the reliability of the procedure proposed in [14]. This method of determining the W value was previously applied to the adsorption systems on the basis of zeolites [3, 4] and yielded the results close to the predictions of other methods.

Figure 3 represents the absolute adsorption isotherms $a = a(p)$ calculated based on $W = 0.246$ cm³/g. The adsorption isotherms $\Gamma = \Gamma(p)$ measured over a broad pressure range (including the high-pressure region) provide more detailed information on the influence of adsorbent on adsorptive than the absolute adsorption isotherms $a = a(p)$. At low equilibrium pressures, the adsorbent produces the strongest effect on the adsorptive; then the adsorption increases with pressure and reaches a maximum at which the forces of attraction between the adsorbate molecules and between the adsorbate and adsorbent molecules is counterbalanced by the forces of repulsion between adsorbate molecules. At still higher pressures, the Gibbs adsorption Γ tends to zero; under these conditions, the average density of adsorbate is equal to that of the equilibrium gas phase. This means that the adsorbent has no effect on the adsorptive. Obviously, the isosteres and isoteric heats of adsorption q_{st}^{Γ} also change.

Figure 4 displays the Gibbs adsorption isotherms. As can be seen, the isotherms are linear in the low-pressure region, up to a coverage of ~1.6 mmol/g; the slope of isotherms is virtually independent of the temperature over this pressure range. The adsorption heats q_{st}^{Γ} calculated by equation (1) are about ~22 kJ/mol (Fig. 5). In going from the side of high pressures, the isosteres are also linear down to 1.2 mmol/g (Fig. 4), with a slope close to zero (Fig. 5). Similar behavior was reported for the N_2–NaA, Kr–NaA, and CH_4–Rho adsorption systems [2, 3, 16]. Probably, the energy of adsorbate–adsorbent interactions and the energy of repulsion between adsorbate molecules in this pressure range take such values that the adsorption heat q_{st}^{Γ} is close to zero. For nonlinear Gibbs adsorption isosteres (Fig. 4), the isosteric heats of adsorption calculated by equation (1) are ambiguous and tend to infinity at certain temperatures and fillings (Fig. 5).

Figure 6 shows that the absolute adsorption isosteres are linear. The isosteric adsorption heat q_{st}^{a} calculated by the equation [17],

$$q_a = -RZ[1-(\bar{V}/V_g)_T](d\ln p/dT^{-1})_a - (dp/dT)_T[V_0 - T(dV_0/dT)_a] \tag{9}$$

($\bar{V}$ is the partial molar volume of adsorbate) is about ~20 kJ/mol at fillings up to ~3.6 mmol/g (10–50 MPa); at larger fillings, the q_{st}^{a} decreases (Fig. 7). The isosteric adsorption heats q_{st}^{a} do not exhibit those peculiarities which are observable for the q_{st}^{Γ} adsorption heats (Fig. 5). This behavior of the Gibbs adsorption heat is due to a specific shape of the $\Gamma = \Gamma(p)$ adsorption isotherms. This can be confirmed in the following way. Using the universal correlation between a and Γ (7) and differentiating it with respect to T and p, we obtain

$$\left|\frac{da}{dp}\right|_T = \left|\frac{d\Gamma}{dp}\right|_T + W\left|\frac{d\rho}{dp}\right|_T + \rho\left|\frac{dW}{dp}\right|_T, \tag{10}$$

$$\left|\frac{da}{dT}\right|_p = \left|\frac{d\Gamma}{dT}\right|_p + W\left|\frac{d\rho}{dT}\right|_p + \rho\left|\frac{dW}{dT}\right|_p. \tag{11}$$

The thermal equations for the Gibbs and absolute adsorption takes the form

$$F(\Gamma, p, T) = 0 \text{ and } \Phi(a, p, T) = 0. \tag{12}$$

This equation in conjunction with the known relationship gives

$$\left|\frac{d\Gamma}{dp}\right|_T\left|\frac{dp}{dT}\right|_\Gamma\left|\frac{dT}{d\Gamma}\right|_p = -1 \text{ and } \left|\frac{da}{dp}\right|_T\left|\frac{dp}{dT}\right|_a\left|\frac{dT}{da}\right|_p = -1. \tag{13}$$

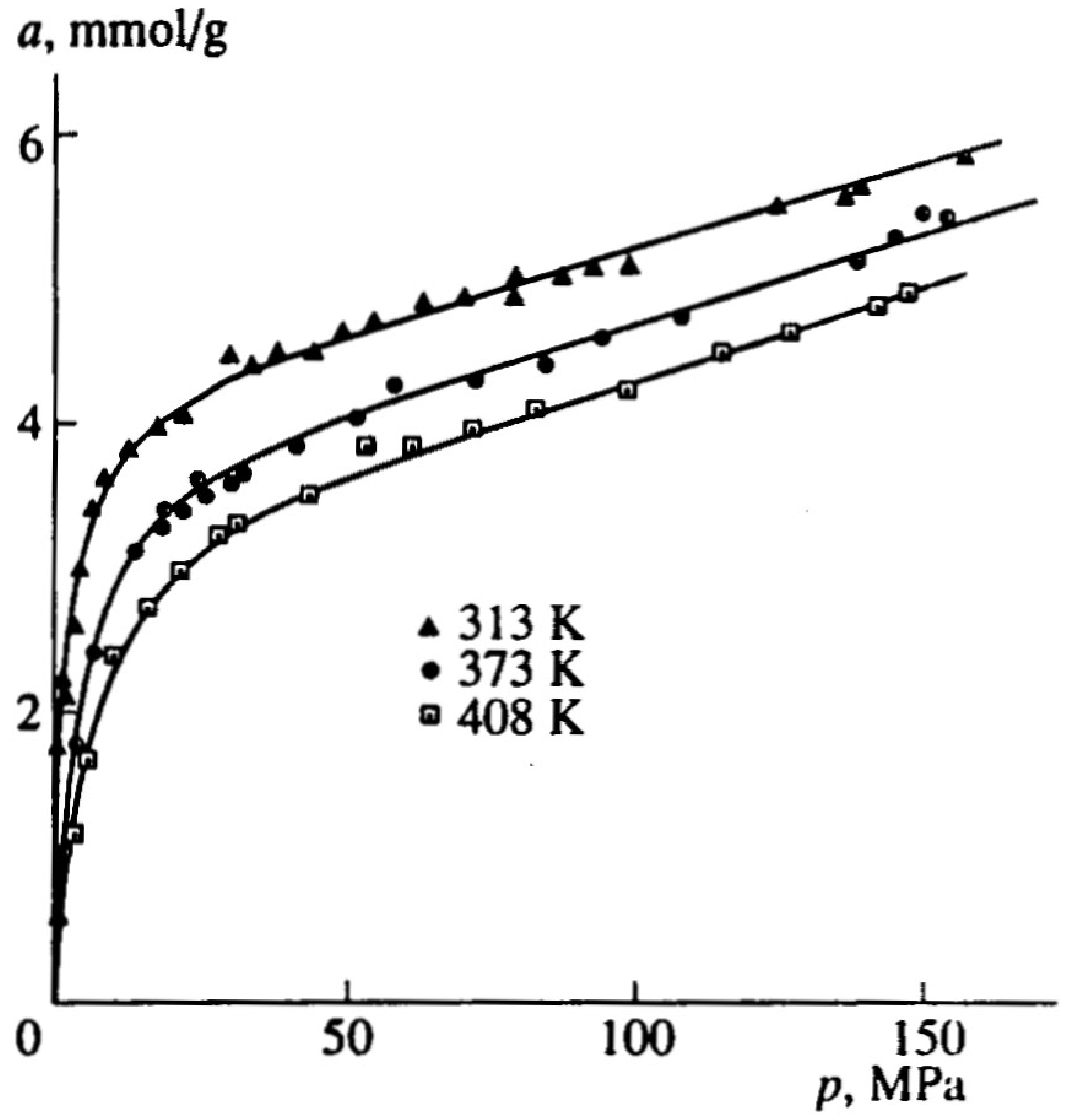

Fig. 3. Absolute adsorption isotherms for methane on CMS activated carbon.

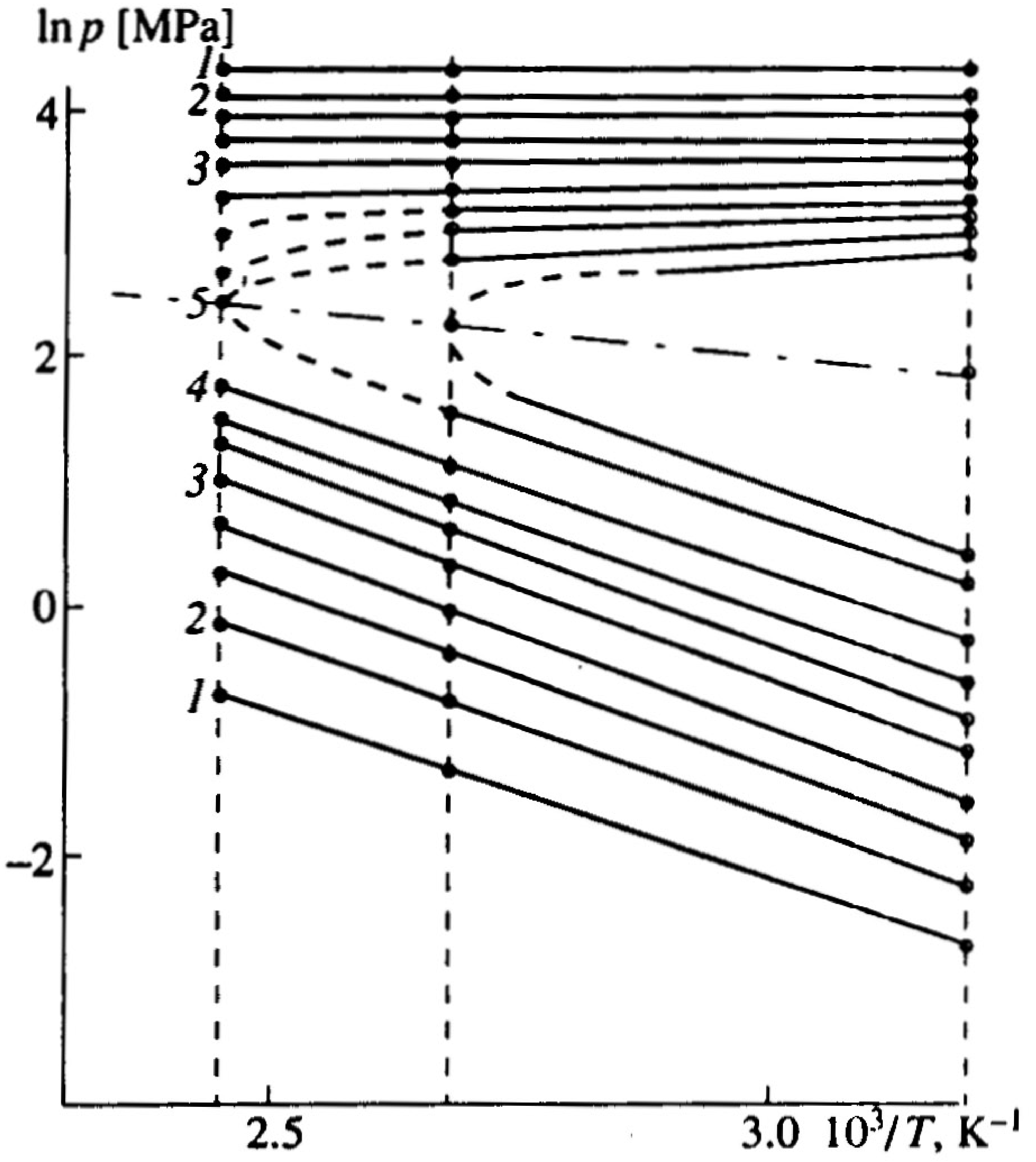

Fig. 4. Isosteres of the Gibbs adsorption for CH_4 on CMS activated carbon at Γ = (*1*) 0.2, (*2*) 0.4, (*3*) 1.0, (*4*) 1.6, (*5*) 2.82.

Solving equations (13) relative to $(d\Gamma/dp)_T$ and $(da/dp)_T$ and substituting the values obtained into equations (10) and (11), we obtain, after simple rearrangements, the following expression relating q_{st}^{Γ} and q_{st}^{a}

$$q_{st}^{\Gamma} = q_{st}^{a}\frac{(da/dp)_T}{(1 - \bar{V}_a/V_g)}\left|\frac{dp}{d\Gamma}\right|_T + TW\left|\frac{dp}{d\Gamma}\right|_T\left[\left|\frac{d\ln p}{dT}\right|_p + \left|\frac{d\ln W}{dT}\right|_p\right]. \tag{14}$$

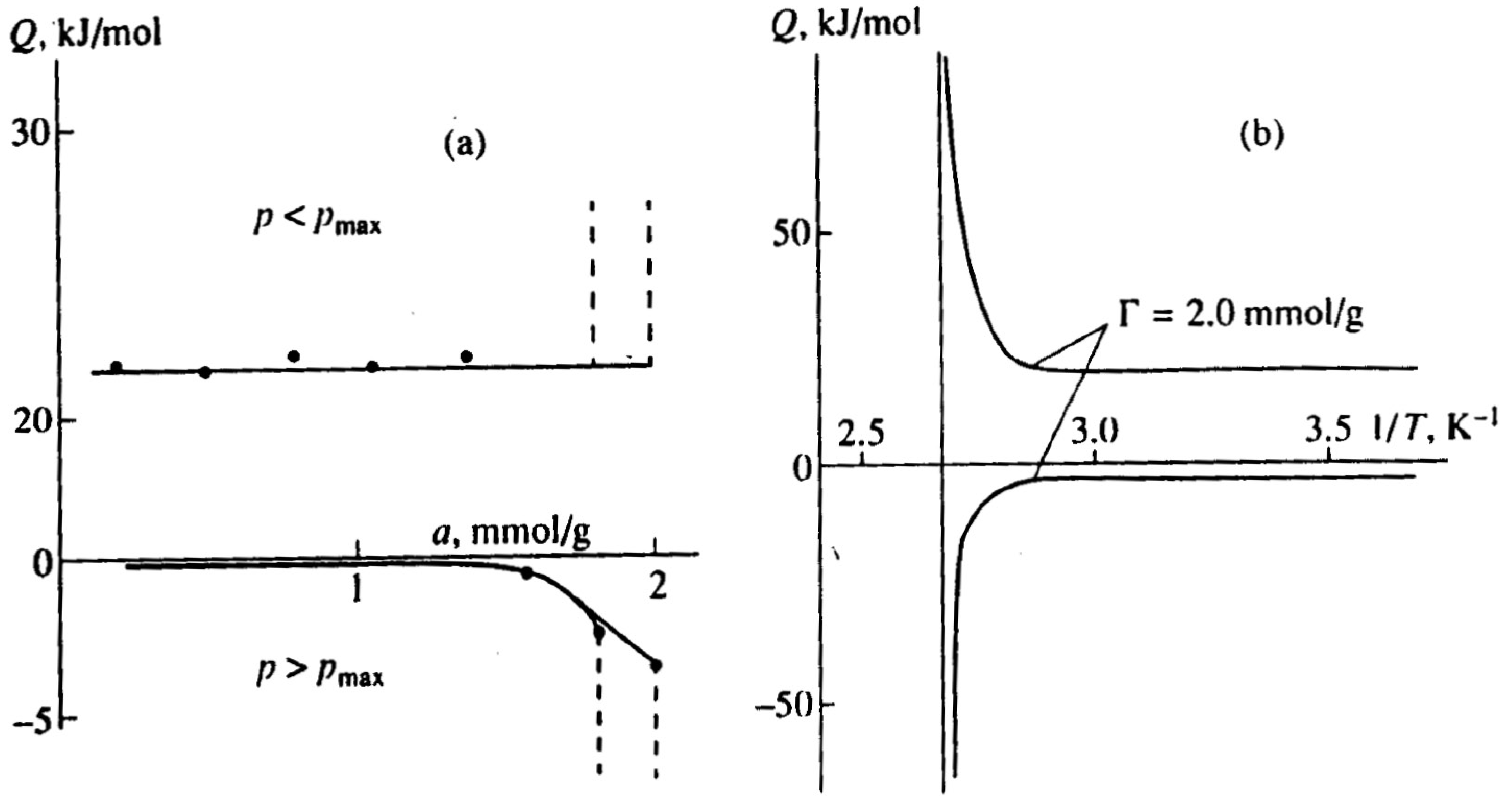

Fig. 5. Isosteric heats of the Gibbs adsorption for CH_4 on CMS activated carbon as functions of (a) filling and (b) temperature.

The derivative of the Gibbs adsorption isotherm is responsible for infinitely high values of the isosteric heat. A similar formula was derived in [18] by a different method.

The obtained heats q_{st}^{a} of adsorption of methane on CMS adsorbent are somewhat higher than those on CaA zeolite. In the latter case, the heat of adsorption varies from 13.4 to 11 kJ/mol as the filling degree is increased from 1 to 3.7 mmol/g [19]. Note that the linear size of the α-cavity in NaA zeolite (L = 0.14 nm [20]) and the average size of the pores in CMS adsorbent (L = 0.8 nm) are commensurate. The difference in the heats of adsorption of methane on the microporous adsorbent and zeolite is due to both the distinctions in structure and, to some extent, in chemical composition. In contrast to the zeolite, in which the electric fields exist [20], the carbonaceous adsorbent attracts methane molecules by means of the dispersion force. The dispersion interaction energy is given by [21]

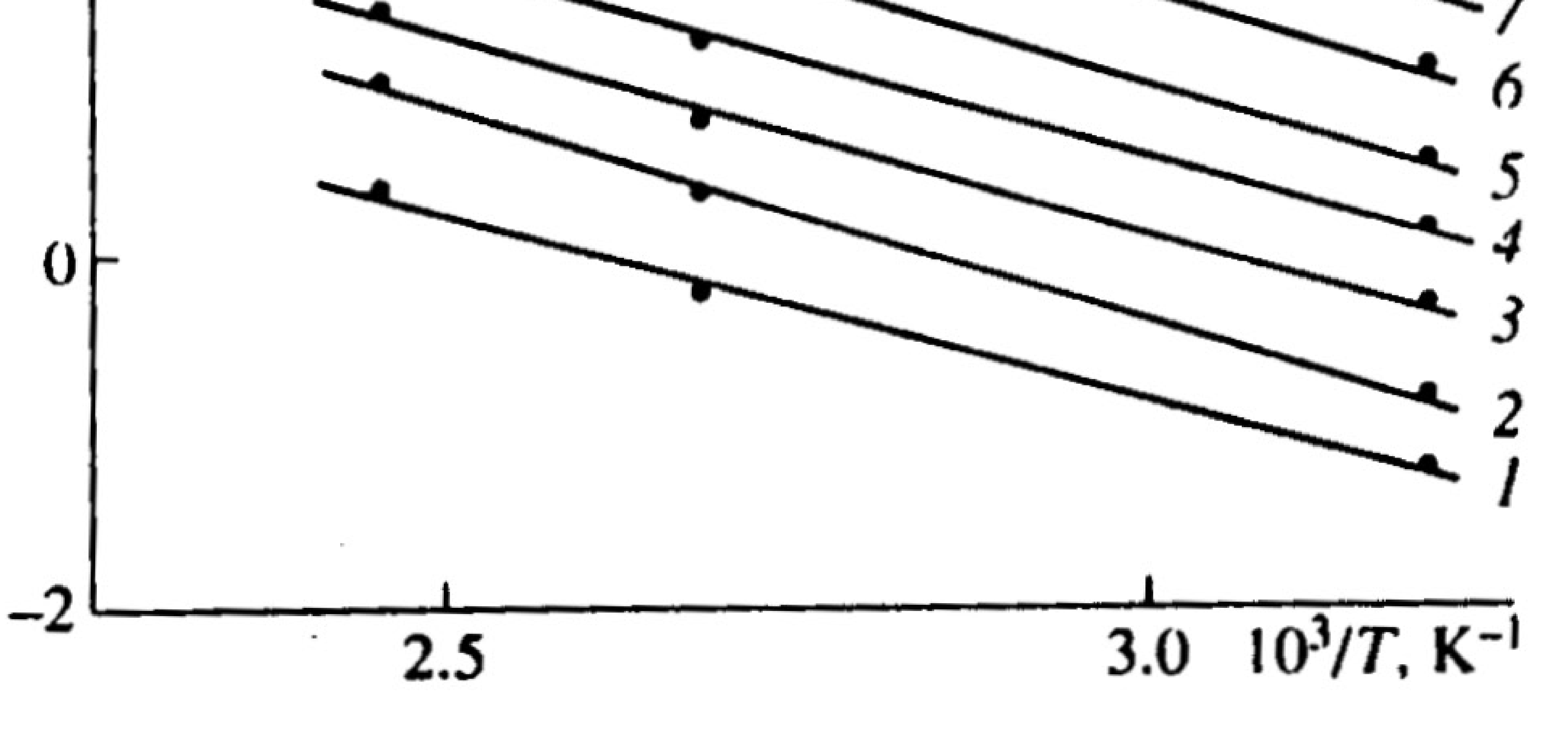

Fig. 6. Isosteres of the absolute adsorption for CH_4 on CMS activated carbon at a: (*1*) 0.8, (*2*) 1.2, (*3*) 1.6, (*4*) 2.0, (*5*) 2.4, (*6*) 2.8, (*7*) 3.2, (*8*) 3.6, (*9*) 4.0, (*10*) 4.4, (*11*) 48, and (*12*) 5.2, mmol/g.

$$E = C\sum_i r_i^{-6}, \quad C = -6mc^2\alpha_1\alpha_2/(\alpha_1/\kappa_1 + \alpha_2/\kappa_2), \tag{15}$$

where C is the dispersion interaction constant, r is the average separation distance between the methane molecules and adsorbent atoms, c is the speed of light in vacuum, α_i and κ_i are the polarizability and magnetic susceptibility of the methane molecule and adsorbent atom, and m is the mass of electron.

The values of α and κ for the carbon atom are smaller than those for the oxygen atom (the most abundant chemical element in the zeolite); this factor reduces the E value for the CH_4–C system, but a higher surface density of carbon atoms of the adsorbent increases E. The radius of the hexagon, a structural element of the carbonaceous adsorbent, is 0.142 nm [11], whereas the distance between the oxygen atoms in the tetrahedral cell of the zeolite is 0.276 nm. The CH_4–C interaction energy increases with decreasing r_i in (15); its value is a sum of the energies of interaction of a methane molecule with the neighboring carbon atoms, whose number can be as high as 6. In contrast to the zeolite, in which the cavities are of the same size, the microporous carbonaceous adsorbent is characterized by a pore size distribution, i.e., pores smaller than the average size (0.8 nm) are available. In this case, the

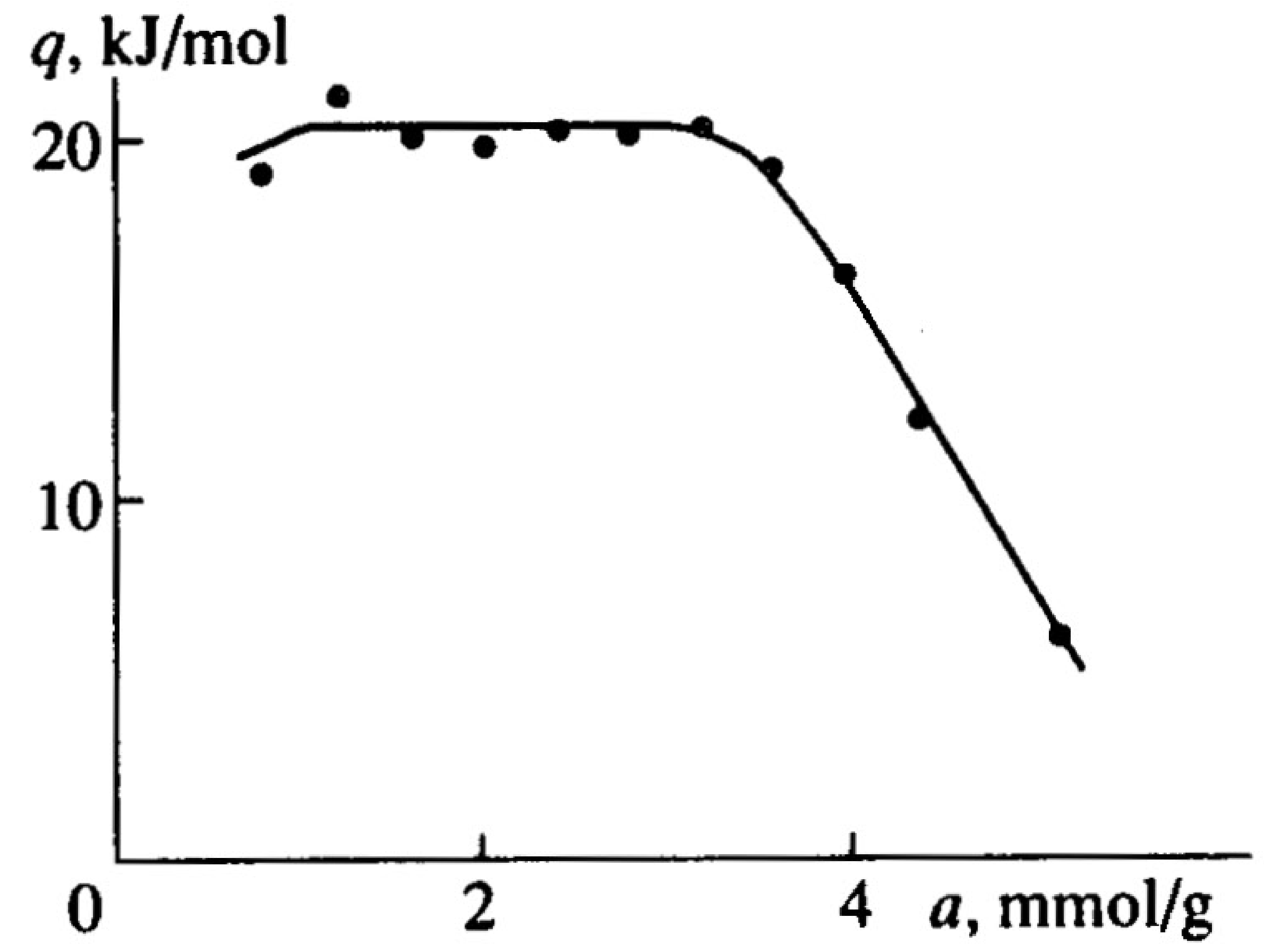

Fig. 7. Isosteric heats of adsorption for CH_4 on CMS activated carbon.

opposite wall contributes to the parameter E to a greater extent than in the case of the zeolite. The total pore volume in CMS adsorbent as measured by the method described in [14] or by the TVFM method is larger (by a factor of ~1.5) than that in the zeolite for various gases [3, 9]. For instance, $W = 0.17$ cm^3/g for Kr [4]. Thus, a larger adsorption volume of CMS microporous carbonaceous adsorbent is primarily responsible for a higher heat of adsorption of methane q_{st}^{a} (by a factor ~1.5) in comparison with the zeolite; this results in higher adsorption values.

To summarize, a comparison of methane adsorption on the zeolite and microporous carbonaceous adsorbent suggests that microporous activated carbons do better as adsorbents of gases.

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