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Modeling CO_2, CO, CH_4, and H_2 sorption equilibrium on NaX and CaA zeolites and activated carbon using the Dubinin–Astakhov equation

©Dmitry S. Dvoretsky[a]✉, Stanislav I. Dvoretsky[a], Evgeniy I. Akulinin[a], Evgeny N. Tugolukov[a], Gleb I. Varnikov[a], Vladimir B. Usachev[b]

[a] *Tambov State Technical University, Bld. 2, 106/5, Sovetskaya St., Tambov, 392000, Russian Federation,*
[b] *JSC Research Institute of Scientific Production Association Luch, Protvino branch, 5, Zheleznodorozhnaya St., Protvino, 142281, Russian Federation*

✉ dvoretsky@yahoo.com

Abstract: In light of the findings from experimental studies, adsorption isotherms were obtained for carbon dioxide, carbon monoxide, methane, and hydrogen gases on industrial adsorbents. A methodology has been put forth for calculating the coefficients of the Dubinin–Astakhov equation based on experimental isotherms. This approach enables the determination of the equilibrium adsorption of components of a hydrogen-containing gas mixture with a high degree of accuracy. The approach includes: calculating the limiting adsorption volume of a given adsorbent and the characteristic adsorption energy of a standard gas (nitrogen) for the specified adsorbent using experimental nitrogen adsorption isotherms obtained at a temperature of 77.3 K in the relative pressure range from 0 to 1 for each of the studied adsorbents, namely: NaX, CaA, SKT-4; determining the calculated values of the affinity coefficients, the exponent, and the thermal coefficient of limiting adsorption in the Dubinin–Astakhov equation (for the temperatures and pressures at which the experimental sorption isotherms of the studied gases were obtained), which minimize the residual between the calculated and experimental isotherms; averaging the obtained values of the affinity coefficients and the exponent. The efficacy of the proposed approach is substantiated by the calculation of the parameters of the Dubinin–Astakhov equation for CO_2, CO, and CH_4 using NaX and CaA zeolites and SKT-4 activated carbon. The root mean square deviation between the calculated and experimental data does not exceed 6.6 % over a wide range of pressures (up to 3.0 MPa) and temperatures (293–353 K) for the studied sorbents (zeolites NaX, CaA, and activated carbon SKT-4).

Keywords: hydrogen-containing gas mixture; adsorbent; adsorption separation; adsorption equilibrium; adsorption isotherm; Dubinin–Astakhov equation; zeolite; activated carbon; root mean square error; maximum deviation.

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Моделирование сорбционного равновесия CO_2, CO, CH_4, H_2 с использованием уравнения Дубинина–Астахова на цеолитах NaX, CaA и активном угле

© Д. С. Дворецкий[a]✉, С. И. Дворецкий[a], Е. И. Акулинин[a], Е. Н. Туголуков[a], Г. И. Варников[a], В. Б. Усачев[b]

[a] *Тамбовский государственный технический университет, ул. Советская, 106/5, пом. 2, Тамбов, 392000, Российская Федерация,*
[b] *АО НИИ НПО «Луч» Протвинский филиал, ул. Железнодорожная, 5, Протвино, 142281, Российская Федерация*

✉ dvoretsky@yahoo.com

Аннотация: По результатам экспериментальных исследований получены адсорбционные изотермы для газов: диоксида углерода, оксида углерода, метана и водорода на промышленных адсорбентах. Предложен подход для расчета коэффициентов уравнения Дубинина–Астахова на основе экспериментальных изотерм, позволяющий

определять величину равновесной адсорбции компонентов водородсодержащей газовой смеси с высокой точностью. Подход включает: расчет значений предельного адсорбционного объема данного адсорбента и характеристической энергии адсорбции стандартного газа (азота) для заданного адсорбента с использованием экспериментальных изотерм адсорбции азота, полученных при температуре 77,3 K в диапазоне относительных давлений адсорбции от 0 до 1 на каждом из исследуемых адсорбентов, а именно: NaX, CaA, СКТ-4; нахождение расчетных значений коэффициентов аффинности, показателя степени, термического коэффициента предельной адсорбции уравнения Дубинина–Астахова (для температур и давлений, при которых получены экспериментальные изотермы сорбции исследуемых газов), обеспечивающих минимальное значение невязки между расчетными и экспериментальными изотермами; усреднение найденных значений коэффициентов аффинности и показателя степени. Эффективность предложенного подхода продемонстрирована на примере расчета параметров уравнения Дубинина–Астахова для CO_2, CO, CH_4 при использовании цеолитов NaX, CaA, активного угля СКТ-4. Среднеквадратическое отклонение между расчётными и экспериментальными данными не превышает 6,6 % в широком диапазоне давлений (до 3,0 МПа) и температур (293…353 K) для изученных сорбентов (цеолиты NaX, CaA, активный уголь СКТ-4).

Ключевые слова: водородсодержащая газовая смесь; адсорбент; адсорбционное разделение; адсорбционное равновесие; изотерма адсорбции; уравнение Дубинина–Астахова; цеолит; активный уголь; среднеквадратическая ошибка; максимальное отклонение.

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1. Introduction

The pressure swing adsorption (PSA) method has become a prevalent technique in the field of chemical technology, particularly in the context of the delivery and storage of pure technical gases, when relatively low production volumes are required. The present study investigates the application of the PSA method in the separation of hydrogen-containing gas mixtures during hydrogen concentration. The PSA method is implemented in the pressure range (30×10^5 Pa) and at temperatures of 293–333 K. The results demonstrate that the PSA method allows for the production of a gas mixture containing up to 99.99 % vol. hydrogen [1–3].

The contemporary design of gas separation facilities that utilize the PSA method has evolved significantly from the past, when the selection of adsorbent layers and the determination of operating modes were done on an intuitive basis. It is critical for developers of such facilities to consider a comprehensive array of interconnected trends to ensure that the plant is as competitive, efficient, flexible, and reliable as possible. The era of empirical selection and trial and error is coming to a close. In the contemporary realm of design, it is imperative that models encompass the entirety of the intricate processes that occur in tandem during the adsorption separation of gas mixtures. These processes are contingent upon variables such as temperature, pressure, the velocities of components within the gas stream and within the adsorbent (micro, meso, and macro pores), and the nature and rate of redistribution of the sorption volume between gases.

In the process of mathematical modeling of sorption processes in PSA units, it is essential to select isotherms that correctly reflect the equilibrium sorption characteristics of the "solid sorbent – absorbed component" system [4–10]. Modern gas separation calculation models are based on two main theoretical approaches to describing adsorption: surface sorption theory and the concept of volumetric filling of micropores. The first includes the fundamental Langmuir equation and its derivatives [2], while the second includes the Dubinin–Astakhov equation [11, 12].

The concept of volumetric filling of micropores provides a more accurate description of the physics of adsorption-desorption processes in microporous adsorbents, as it takes into account the specific state of the adsorbate, close to the condensed phase, and the energy heterogeneity of micropores [3, 11].

It must be acknowledged that the implementation of both methodologies necessitates the acquisition of experimental adsorption isotherms, their linearization, and the subsequent calculation of the corresponding coefficients derived from the linear forms of the isotherms. Consequently, the coefficients of the equations are derived by solving the inverse problem based on experimental data.

The primary benefit of the Dubinin–Astakhov equation over the Langmuir equation is the classification of parameters into two distinct categories: those that delineate the adsorbent (W_0, microporous volume; E_0, characteristic adsorption energy of standard gas) and those that delineate the adsorbate (φ_i, affinity coefficient; n_i, empirical

exponent; α_i, thermal coefficient of maximum adsorption). This approach enables the determination of the adsorbent constants (W_0, E_0) once from the isotherm of the reference gas. Subsequently, the parameters specific to each adsorbate (φ_i, n_i, α_i) can be determined to describe the isotherms of other gases.

According to the sources cited [1, 11, 13, 14], the ranges of values for the coefficients of the Dubinin–Astakhov equation have been established. These ranges are [0.8–4.0] for the coefficient φ_i and [1–6] for the coefficient n_i. These values are applicable to the most frequently used PSA zeolite adsorbents (NaX, CaA, and activated carbons) in adsorbers [15–22]. The temperature range for sorption processes (293–333 K) for gases included in a hydrogen-containing gas mixture (CO_2, CO, CH_4, H_2) significantly exceeds the critical temperatures of the following components: carbon monoxide (133 K), methane (190 K), hydrogen (33 K). In this regard, it is plausible that the values of the thermal coefficient of maximum adsorption, α_i, incorporated within the Dubinin-Astakhov equation, may exhibit deviation from the calculated values, as delineated in the methodology [11], which is applicable within the temperature range extending from the normal boiling point to the critical temperature.

Different estimates of the values of W_0 and E_0 for adsorbents of the same type (NaX, CaA, activated carbon) [1–3, 11] are explained by the variety of manufacturers and technological features of their production. There is also no single approach to calculating the values of affinity coefficients φ_i. The most common methods include finding the ratio of the parachors of the test and standard gases [1]. According to the Sugden–Quayle method [13], the parachor of the adsorbed gas ω can be calculated as the sum of the structural components of the parachors of the atoms that make up the molecule of the adsorbed gas. According to the McGowan method [14], the parachor of the adsorbed gas ω can be defined as the sum of the structural components of the parachors of the atoms ω_i that make up the molecule of the adsorbed gas, minus the number of bonds in the gas molecule.

Given the ranges of variation that have been described and the options for calculating the coefficients of the Dubinin–Astakhov equation, it is evident that satisfactory precision in characterizing the equilibrium conditions of hydrogen-containing gas mixture components can be attained by developing an approach that encompasses the acquisition and processing of experimental adsorption-desorption isotherms.

The objective of this study is to develop an approach to enhancing the accuracy of describing the isotherms of the adsorption process of hydrogen-containing gas mixture components on microporous adsorbents.

2. Methods and Materials

2.1. Initial materials

Industrial microporous zeolites NaX and CaA [23] and activated carbon SKT-4 (sulfurous potassium peat coal) [24] were utilized as adsorbents.

2.2. Theoretical approaches

A proposed approach is outlined, with the primary objective being the identification of the coefficients of the Dubinin–Astakhov equation that guarantee minimal values for the root mean square error (RMSE) between calculated and experimental values of equilibrium adsorption within the operational temperature and pressure ranges of 293–333 K and 30×10^5 Pa, correspondingly.

The approach encompasses the calculation of the maximum adsorption volume (W_0) and the characteristic adsorption energy (E_0) of a given adsorbent with N_2 using experimental N_2 isotherms at $T = 77.3$ K in the range $P/P_s = 0$–1 for each of the adsorbents under study (NaX, CaA, SKT-4). This approach also involves finding the calculated values of the affinity coefficients φ_i, the exponent n_i, and the thermal coefficient of maximum adsorption α_i of the Dubinin–Astakhov equation (for temperatures and pressures at which experimental adsorption isotherms of the studied gases were obtained), ensuring a minimum discrepancy between the calculated and experimental isotherms. Finally, the approach entails averaging the found values of φ_i and n_i.

To evaluate the effectiveness of the proposed approach, we compared the adsorption values using the φ_i and n_i values found in the previous step and the φ_i values determined from the literature [1, 13, 14] for $n_i = 1, 2, 3$.

Dubinin–Astakhov equation and the dependencies included in it:

$$a_i^* = a_{0i} \exp\left[-\left(\frac{RT \lg\left(P_{si}/P\right)}{\varphi_i E_0} \right)^{n_i} \right]; \qquad (1)$$

$$a_{0i} = \frac{W_0}{V_i^*}\exp\left[-\alpha_i\left(T - T_{\mathrm{b},i}\right)\right]; \quad (2)$$

$$V_i^* = \frac{M_{\mathrm{g},i}}{\rho_i^*}; \quad (3)$$

$$\rho_i^* = 10^3 \rho_{\mathrm{b},i} 10^{-0.434\alpha_i\left(T - T_{\mathrm{b},i}\right)}; \quad (4)$$

$$\alpha_i = \frac{\lg\left(\frac{\rho_{\mathrm{b},i}}{\rho_{\mathrm{cr},i}^*}\right)}{0.434\left(T_{\mathrm{cr},i} - T_{\mathrm{b},i}\right)}; \quad (5)$$

$$\rho_{\mathrm{cr},i}^* = \frac{M_{\mathrm{g},i}}{b_i}; \quad (6)$$

$$b_i = \frac{RT_{\mathrm{cr},i}}{8\cdot 10^{-3} P_{\mathrm{cr},i}}; \quad (7)$$

$$P_{\mathrm{s},i} = \frac{\exp\left(\frac{A_i - F_i}{T - C_i}\right)}{760} 10^5, \quad (8)$$

where a_{0i} is the maximum adsorption value of the i-th component, mol·kg^{-1}; P_{si} is the saturation pressure of the pure adsorbent, Pa; φ_i is the affinity coefficient characterizing the affinity of the adsorbed gas to the standard (N_2); E_0 is thecharacteristic adsorption energy of the standard gas N_2, J·mol^{-1}; n_i is and exponent; W_0 is micropore volume of the adsorbent, cm^3·g^{-1}; V_i^* is molar volume of the adsorbate, m^3·mol^{-1}; α_i is a thermal coefficient of maximum adsorption, K^{-1}; T is adsorption temperature, K; $T_{\mathrm{b},i}$ – boiling temperature of the i-th component of the gas mixture, K; $M_{\mathrm{g},i}$ – molar mass of the i-th component of the gas mixture, g·mol^{-1}; ρ_i^* – adsorbate density at a temperature T above $T_{\mathrm{b},i}$, kg·m^{-3}; $\rho_{\mathrm{b},i}$ – gas density at boiling temperature, kg·m^{-3}; T – adsorption temperature, K; $T_{\mathrm{cr},i}$ – critical temperature of the i-th component of the gas mixture, K; $\rho_{\mathrm{cr},i}^*$ – adsorbate density at critical temperature, kg·m^{-3}; b_i – molar volume constant, m^3·mol^{-1}; R – universal gas constant, J·(mol·K)$^{-1}$; $P_{\mathrm{cr},i}$ – critical pressure of the i-th component of the gas mixture, Pa; A_i, F_i, C_i – Antoine equation constants.

Table 1. Parameter values for calculations with the use of the Dubinin–Astakhov equation

Parameter	CH_4	CO_2	CO	H_2
$M_{\mathrm{g},i}$, g·mol^{-1}	16.04	44.01	28.01	2.02
$\rho_{\mathrm{b},i}$, g·cm^{-3}	0.43	0.78	0.78	0.07
$T_{\mathrm{b},i}$, K	111.7	197.7	81.6	20.4
$T_{\mathrm{cr},i}$, K	190.6	304.2	132.9	33.2
$P_{\mathrm{cr},i}$, ×10^5 Pa	45.4	72.8	34.9	12.8
A_i	15.22	22.59	14.37	13.63
F_i	897.84	3103.39	530.22	164.90
C_i	7.16	0.16	13.15	3.19

The values of the coefficients of the Dubinin–Astakhov equations (1) – (8), as determined on the basis of reference data, are presented in Table 1 [13].

The values of parameters W_0, E_0, φ_i, n_i, α_i were determined on the basis of experimental data.

The calculation of the values of the maximum adsorption volume W_0 and the characteristic adsorption energy E_0 of the standard gas N_2 was performed using the experimental adsorption isotherm of the standard gas N_2 in the range $P/P_s = 0$–1 for each adsorbent (NaX, CaA, SKT-4). The N_2 isotherms at $T = 77.3$ K in the range $P/P_s = [0–1]$ were obtained using the Autosorb IQ Nova 1200e analyzer (Quantochrome Instruments), after which W_0 and E_0 were calculated using the method described in [11]. Next, a combination of values $[\varphi_i, n_i]$ was selected at which the smallest root mean square deviation δ of the experimental and calculated isotherms was observed at k mean values $[\overline{\varphi}_j, \overline{n}_j]$, where k is the number of experimental isotherms. The values $\overline{\varphi}_j, \overline{n}_j$ were determined as the arithmetic mean φ_j, n_j found for: three temperatures ($k = 3$, $T = 293$, 313, 333 K), for the boundary values of the interval ($k = 2$, $T = 293$, 333 K), for the average temperature ($k = 1$, $T = 313$ K).

The parameters φ_j, n_j, α_i of the Dubinin–Astakhov equation were determined for three temperatures (293, 313, 333 K) based on the results of solving the problem of minimizing the discrepancy

function between the values calculated according to equations (1), (2) with the found coefficients φ_j, n_i, α_i and the experimental $a_i^{*,e}(P,T)$ isotherms. The problem of minimizing the discrepancy function is formulated as follows. For the *i*-th component of the gas mixture, it was necessary to determine the parameters φ_j, n_j and α_i in equations (1) and (2) at temperature T_j, at which there was achieved a minimum value of the root mean square deviation δ between the experimental $a_i^{*,e}$ and calculated $a_i^{*,c}$ values of equilibrium adsorption at given *P*, T_j:

$$\delta_j\left(\hat{a}_i^*\right) = \min_{\varphi_j, n_j, \alpha_j} \delta_j\left(a_i^*\left(\varphi_j, n_j, \alpha_i\right)\right), \qquad (9)$$

where δ is calculated using the formula

$$\delta = \sqrt{\frac{1}{N}\sum_{l=1}^{m}\left(\frac{a_l^{*,e} - a_l^{*,c}}{a_l^{*,e}}\right)} 100\%, \qquad (10)$$

where *N* is the total number of experimental points *l*.

The problem (9), (10) was solved in the MatLab software environment using the fmincon function [25].

The experimental isotherms $a_i^{*,e}\left(P,T_j\right)$ for CO_2, CO, CH_4, H_2 at $T_j = 293$, 313, 333 K in the range $P_i = [1–30]\times10^5$ Pa were obtained using the ISorb HP1 analyzer (Quantochrome Instruments).

The adsorption values were determined using φ_i data from [1] and calculated according to the Sugden–Quayle [13] and McGowan [14] methods at $n_i = 1, 2, 3$, with α_i values determined according to the formula (5).

3. Results and Discussion

Experimental adsorption isotherms for the model gas (nitrogen) in the relative pressure range $P/P_s = [0–1]$ at 77.3 K are shown in Fig. 1*a*, *c*, *e*, and the isotherms in rectifying coordinates $\left[\lg a_i^* - (\lg P_{0i}/P)^{n_{N_2}^*}\right]$ – in Fig. 1*b*, *d*, *f*.

The verification using Fisher criterion at a significance level of 5 % confirmed that the experimental N_2 sorption isotherms on NaX, CaA, and SKT-4 were adequately described by the linear dependencies (Fig. 1*b*, *d*, *f*).

Table 2 presents the calculated values of W_0 and E_{0,N_2} obtained by processing the linearized adsorption isotherms (Fig. 1).

The CO_2, CO, CH_4, H_2 sorption regions limited by experimental isotherms at $T = 293$ K (upper line) and $T = 333$ K (lower line) in the range $P_i = [1–30]\times10^5$ Pa are shown in Fig. 2.

For NaX and CaA zeolites, the CO_2 isotherms are extremely steep within the initial pressure range of 0 to 1×10^5 Pa. After this range, a rapid decrease in the slope of the isotherms is observed within the range of 1×10^5 Pa to 10×10^5 Pa (see Fig. 2*a*, *b*). At $P > 10\times10^5$ Pa, the slope of the isotherm becomes minimal and practically ceases to change. An increase in the adsorption value from $P = 10\times\times10^5$ Pa to $P = 30\times10^5$ Pa (a threefold increase in pressure) leads to an increase in *a* of only 5–10 % for NaX and 10–15 % for CaA (Fig. 2*a*, *b*). The CH_4 and CO isotherms on NaX and CaA are flatter than the CO_2 isotherms. The CH_4 and CO isotherms on NaX are less convex than those on CaA. The CO_2, CO, and CH_4 sorption isotherms on SKT-4 are flat across the entire pressure range (up to 30×10^5 Pa).

Analysis of the isotherm changes shown in Fig. 2 revealed that the most significant change in equilibrium sorption values *a* occurs when *T* changes from 293 to 333 K for CO_2 on SKT-4 (up to 32 %) and for CH_4 on CaA (up to 22 %). The CH_4 and CO sorption areas on NaX almost completely overlap (Fig. 2*a*), while they partially overlap on CaA (Fig. 2*b*). The H_2 isotherms are close to linear over the entire *P* range ($1–30\times10^5$ Pa) on NaX, CaA, and SKT-4.

The values of the parameters $\overline{\varphi}_j, \overline{n}_j$, α_i, calculated at different *k* based on solving equations (12) and (13), are presented in Table 3.

Analysis of the ranges of values $\overline{\varphi}_j, \overline{n}_j$, showed that the greatest deviation $\overline{\varphi}_j$ from the arithmetic mean values calculated at $k = 1, 2, 3$, is observed for CO_2 on all adsorbents: 3.8 % on NaX, 9.5 % on CaA, 1.4 % on SKT-4. It can be assumed that this is due to the large angle of inclination of CO_2 isotherms on these adsorbents compared to CO, CH_4, and H_2. No clear trend is observed for $\overline{n}_j$, and the maximum deviation from the mean value is 5.0 % for CO_2 on CaA, 3.0 % for CH_4 on NaX, and 1.54 % for H_2 on SKT-4 (Fig. 3).

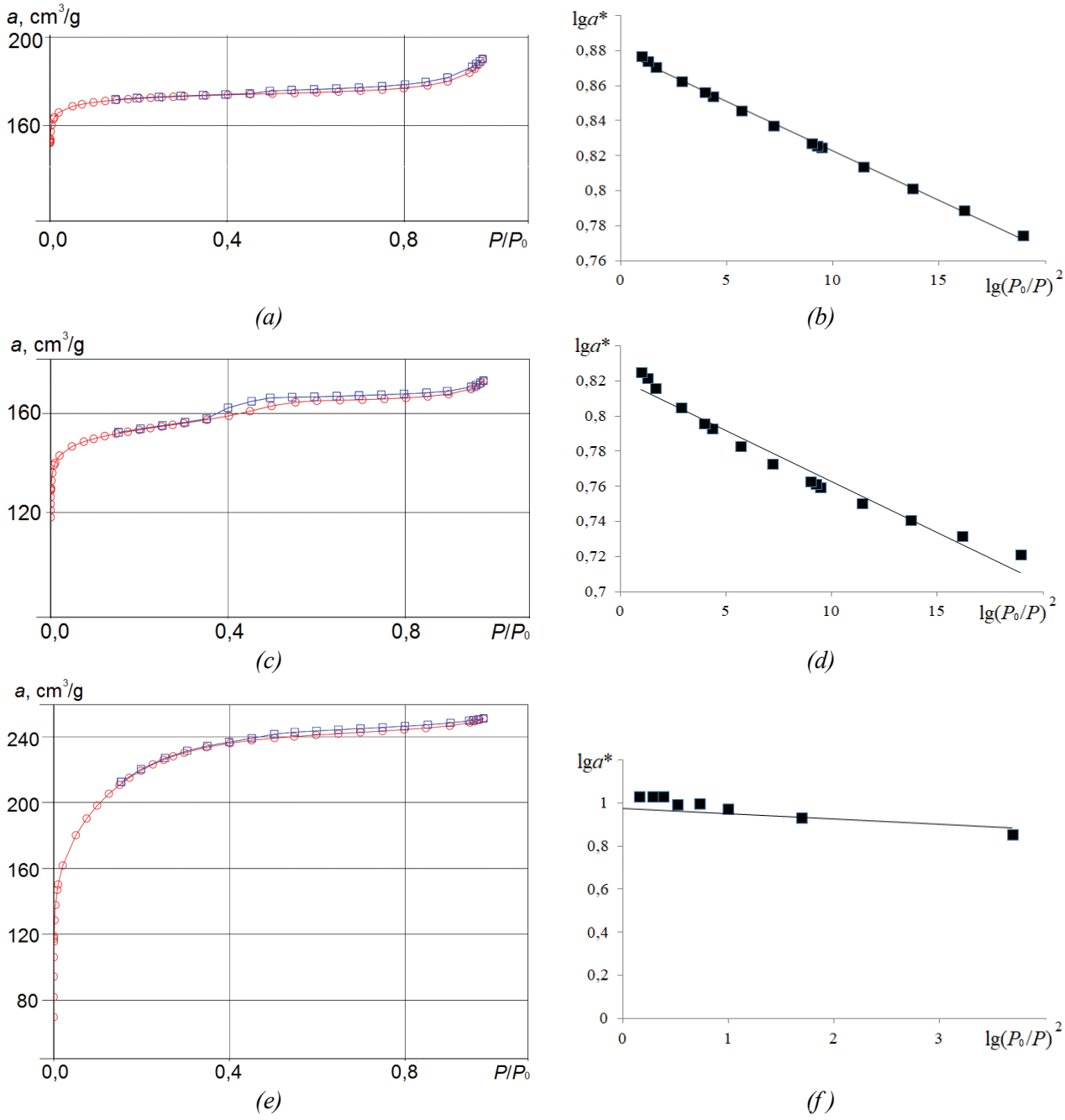


Fig. 1. Experimental sorption isotherms of model gas (nitrogen):
a, *b* on NaX zeolite; *c*, *d* on CaA zeolite; *e*, *f* on SKT-4 activated carbon; *b*, *d*, *f* in rectifying coordinates

Table 2. Linear equations of N_2 isotherms and values of W_0 and E_0

Adsorbent	Linear equation of the isotherm	W_0, $cm^3 \cdot g^{-1}$	E_0, $J \cdot mol^{-1}$
NaX	$\lg a^*_{N_2} = 0.8793 - 0.0057\left(P_{0,N_2}/P\right)^{2,1}$	0.265	12834
CaA	$\lg a^*_{N_2} = 0.8210 - 0.0058\left(P_{0,N_2}/P\right)^{2,3}$	0.230	12796
SKT-4	$\lg a^*_{N_2} = 0.9214 - 0.0208\left(P_{0,N_2}/P\right)^{1,8}$	0.293	6731

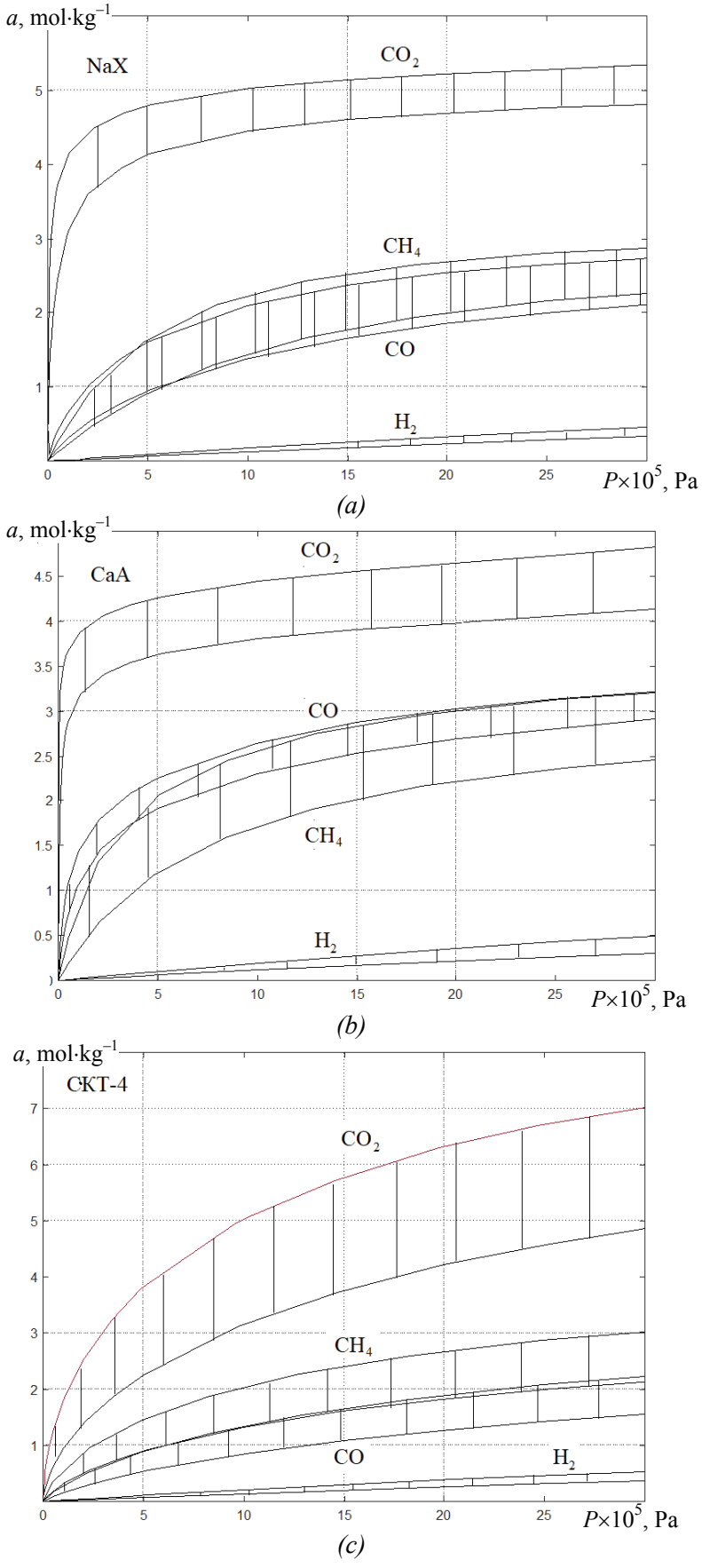


Fig. 2. Experimental adsorption isotherms of components of a hydrogen-containing gas mixture on: *a* – NaX zeolite; *b* – CaA zeolite; *c* – activated carbon SKT-4

Table 3. Values of the coefficients of equations (1) and (2) for different calculation options

Gas	k	$\overline{\varphi}_j$			$\overline{n}_j$			$\alpha_i \times 10^3$		
		NaX	CaA	SKT-4	NaX	CaA	SKT-4	NaX	CaA	SKT-4
CH_4	3	1.17	1.14	1.36	3.01	2.64	1.88	2.30	1.60	1.70
	2	1.16	1.14	1.35	2.96	2.65	1.88	2.20	1.50	1.70
	1	1.21	1.13	1.37	3.12	2.63	1.89	2.50	1.80	1.80
CO	3	0.90	1.46	1.27	2.10	2.54	1.81	1.70	1.50	2.00
	2	0.90	1.46	1.28	2.09	2.55	1.83	1.70	1.50	2.00
	1	0.91	1.47	1.25	2.12	2.54	1.79	1.70	1.50	1.90
CO_2	3	3.82	4.47	1.43	3.30	3.01	1.70	0.50	0.31	2.60
	2	3.74	4.21	1.43	3.24	2.92	1.69	0.50	0.41	2.70
	1	4.00	4.99	1.46	3.33	3.19	1.73	0.60	0.11	2.50
H_2	3	0.30	0.29	0.56	0.92	0.89	0.87	0.06	0.02	0.02
	2	0.30	0.30	0.56	0.92	0.90	0.87	0.07	0.02	0.02
	1	0.30	0.29	0.55	0.91	0.86	0.85	0.03	0.03	0.02

Based on the analysis of maximum root mean square deviations δ and maximum discrepancies Δ, acceptable accuracy in calculating equilibrium conditions for CO_2, CO, CH_4, and H_2 on NaX, CaA, and SKT-4 requires three experimental isotherms obtained at the boundaries (293 and 333 K) and in the middle (313 K) of the sorption process temperature range.

Despite the small values of δ for H_2, the analysis shows that the maximum deviations Δ between the experimental and calculated data exceed 10 % for all adsorbents. This renders the proposed approach unusable for calculating equilibrium adsorption values for H_2 in engineering calculations.

Analysis of the maximum deviations of H_2 adsorption isotherms at 293 and 333 K from the average values (Fig. 2, Table 4) showed that they range from 14 to 18 %. Therefore, based on the experimental isotherms, formal linear dependencies were obtained for the temperature range 293–333 K, which for NaX have the form:

$$a^*_{H_2} = (462 - T)\,10^{-9}\,P_{H2}, \qquad (11)$$

for CaA

$$a^*_{H_2} = (642 - 2T)\cdot 10^{-9} P_{H2}; \qquad (12)$$

for SKT-4

$$a^*_{H_2} = (942 - 2.6T)\cdot 10^{-9} P_{H2}. \qquad (13)$$

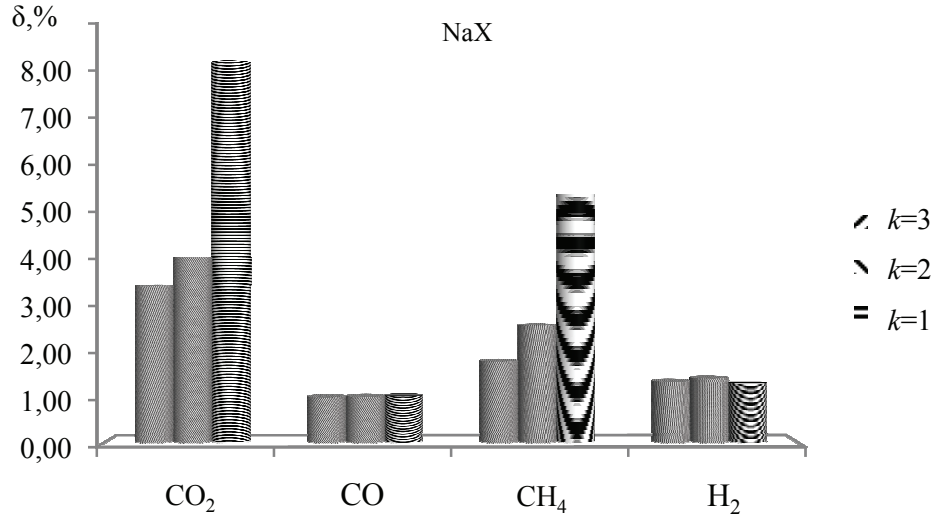
The values of φ_i, n_i found using the proposed approach, at which the smallest root mean square deviation of the calculated and experimental data was observed, are presented in Table 4.

Analysis of the data in Table 4 showed that, when calculating the equilibrium conditions for CO_2, CH_4, and CO on NaX and SKT-4 adsorbents at 353 K (which exceeds the upper limit of the experimental data, 333 K), the equilibrium adsorption value prediction remains acceptable for CO_2 and CO on NaX and SKT-4. However, for CH_4 on NaX and SKT-4, the maximum deviation exceeds 10 %.

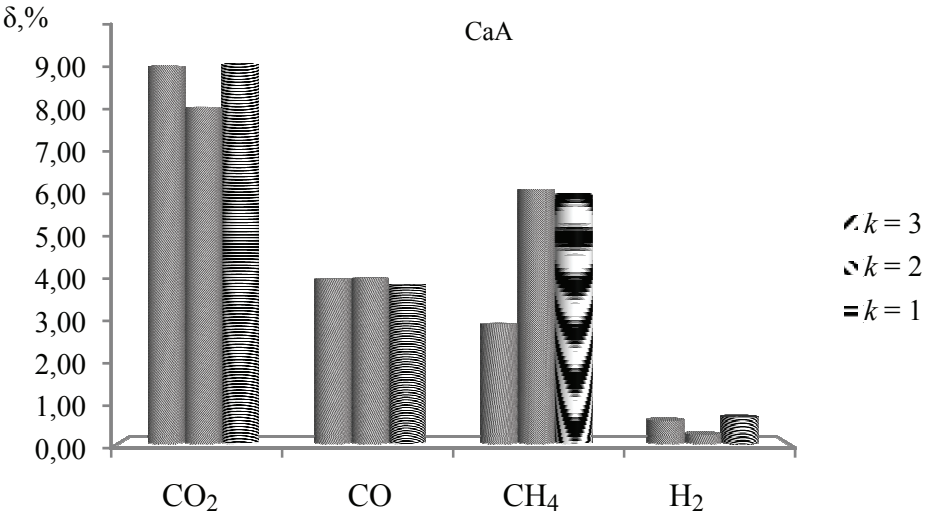
The results of calculating the parameter φ_i values according to the method [1], the Sugden–Quayle [13], and the McGowan [14] methods are presented in Table 5.

As shown in Table 5, the calculated values of the affinity coefficient, φ_i, vary significantly. For CO_2, φ_{CO_2} ranges from 1.25 to 1.40 (±5.6 %) on SKT-4 and from 1.29 to 2.31 (±71.6 %) on NaX and CaA zeolites. For CO, φ_{CO} varies from 0.61 to 1.03 (±34.5 %) on SKT-4 and NaX and CaA zeolites. For CH_4, φ_{CH_4} varies from 1.22 to 2.02 (±34.0 %) on SKT-4 and NaX and CaA.

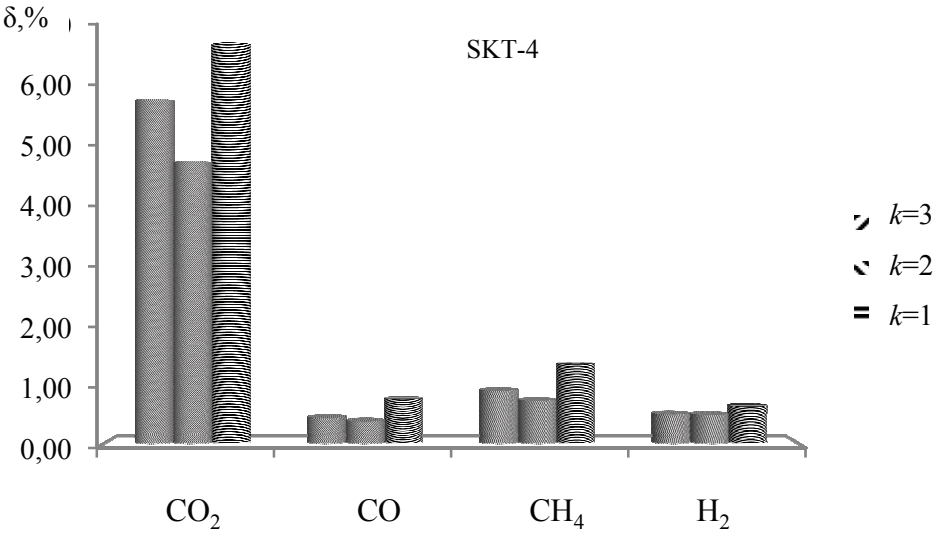
The values of φ_i calculated using the proposed approach align well with the intervals found for CH_4 on SKT-4 (Table 4). The values of φ_i for CO_2 and CO on SKT-4 are close to the upper limits of the intervals. On zeolites, the values of φ_i for CO and CH_4 on NaX and CaA are consistent with the found intervals.



(a)



(b)



(c)

Fig. 3. Maximum values of the root mean square error:
a – on NaX zeolite; *b* – on CaA zeolite; *c* on SKT-4 activated carbon

Table 4. Root mean square deviations of calculations using the Dubinin–Astakhov equation with the coefficients found in equations (1) and (2)

Adsorbent	W_0, $cm^3 \cdot g^{-1}$	E_0, $J \cdot mol^{-1}$	Gas	φ_i	n_i	$\alpha_i \times 10^3$, K^{-1}	Error, % at T, K							
							293		313		333		353	
							δ^*	Δ	δ^*	Δ	δ^*	Δ	δ^*	Δ
NaX	0.265	12834	CO_2	3.82	3.30	0.5	3.4	4.3	4.7	2.3	5.8	6.0	6.3	8.6
			CO	0.90	2.10	1.7	1.0	0.2	0.1	0.1	0.1	0.7	1.4	5.8
			CH_4	1.17	3.01	2.3	0.6	4.0	0.9	4.8	1.8	8.7	4.3	13.4
CaA	0.230	12796	CO_2	4.47	3.01	0.31	4.7	9.1	2.7	3.5	4.8	0.3	n/d	n/d
			CO	1.47	2.54	1.5	0.5	3.8	0.1	1.0	0.5	0.7	n/d	n/d
			CH_4	1.14	2.64	1.6	0.9	4.5	2.9	8.4	0.1	2.0	n/d	n/d
SKT-4	0.293	6731	CO_2	1.43	1.69	2.7	4.8	4.8	0.6	2.4	1.8	1.5	3.9	9.2
			CO	1.28	1.83	2.0	0.4	3.6	0.1	1.6	0.4	5.3	1.4	9.7
			CH_4	1.35	1.88	1.7	0.9	2.8	0.5	3.4	0.8	5.0	3.1	11.7

Table 5. The values of φ_i when using different calculation methods

Method	SKT-4						NaX/CaA					
	Gas	C	ω_i	l/*s*	ω	φ	Gas	*C*	ω_i	l/*s*	ω	φ
Keltsev [1]	CH_4	n/d	n/d	n/d	n/d	1.52	CH_4	n/d	n/d	n/d	n/d	1.52
	CO_2	n/d	n/d	n/d	n/d	1.25	CO_2	n/d	n/d	n/d	n/d	1.25
	CO	n/d	n/d	n/d	n/d	0.61	CO	n/d	n/d	n/d	n/d	0.61
	N_2	n/d	n/d	n/d	n/d	1.00	N_2	n/d	n/d	n/d	n/d	1.00
Sugden–Quayle [13]	CH_4	C	9.00	1	71	2.02	CH_4	C	9.00	1	71	2.02
		H	15.5	4				H	15.5	4		
	CO_2	C	9.00	1	49	1.40	CO_2	C	9.00	1	49	1.40
		O	20.0	2				O	20.0	2		
	CO	C	9.00	1	29	0.83	CO	C	9.00	1	29	0.83
		O	20.0	1				O	20.0	1		
	N_2	N	17.5	2	35	1.00	N_2	N	17.5	2	35	1.00
McGowan [14]	CH_4	C	0.89	4	1.418	1.22	CH_4	C	0.89	4	1.418	1.22
		H	0.47					H	0.47			
	CO_2	C	0.89	2	1.494	1.29	CO_2	C	0.89	2	1.494	1.29
		O	0.64					O	0.64			
	CO	C	0.89	1	1.192	1.03	CO	C	0.89	1	1.192	1.03
		O	0.64					O	0.64			
	N_2	N	0.75	1	1.162	1.00	N_2	N	0.75	1	1.162	1.00

N o t e : ω – parachor; *C* – gas molecule component; *l* – number of atoms of the component in the molecule (method [13]); *s* – number of bonds in the molecule (method [14]); n/d – no data available.

However, the values of φ_i for CO_2 on NaX and CaA, as well as for CO on CaA, are above the found intervals. The indicated deviations from the φ_i value ranges found in the literature for zeolites (Table 5) are observed for extremely steep isotherms in the initial pressure range (CO_2 on NaX and CaA and CO on CaA).

Table 6. Comparison of errors in calculating equilibrium adsorption value at 293 K

Adsorbent	W_0, $cm^3 \cdot g^{-1}$	E_0, $J \cdot mol^{-1}$	Gas	Method	φ_i	n_i	$\alpha_i \times 10^3$, K^{-1}	δ^*, %
NaX	0.265	12834	CO_2	SQ	1.40	2.00	0.5	17.40
				p/a	3.82	3.30	0.5	3.40
			CO	McG	1.03	1.00	1.7	7.70
				p/a	0.90	2.10	1.7	0.98
			CH_4	McG	1.22	2.00	2.3	2.90
				p/a	1.17	3.01	2.3	0.61
CaA	0.230	12796	CO_2	SQ	1.40	2.00	0.31	17.40
				p/a	4.47	3.01	0.31	4.68
			CO	McG	1.03	1.00	1.9	7.70
				p/a	1.47	2.54	1.5	0.50
			CH_4	K	1.34	3.00	1.6	0.50
				p/a	1.14	2.64	1.6	0.92
SKT-4	0.293	6731	CO_2	SQ	1.40	2.00	2.7	17.40
				p/a	1.43	1.69	2.7	4.75
			CO	McG	1.03	1.00	2.0	7.70
				p/a	1.28	1.83	2.0	0.37
			CH_4	McG	1.22	2.00	1.7	2.90
				p/a	1.35	1.88	1.7	0.89

N o t e : K – Keltsev [1] method; SQ – Sugden-Quayle method; McG – McGowan method; p/a – results when using the proposed approach.

Table 7. Comparison of errors in calculating equilibrium adsorption value at 333K

Adsorbent	W_0, $cm^3 \cdot g^{-1}$	E_0, $J \cdot mol^{-1}$	Gas	Method	φ_i	n_i	$\alpha_i \times 10^3$, K^{-1}	δ^*, %
NaX	0.265	12834	CO_2	SQ	1.40	2.00	0.5	48.30
				p/a	3.82	3.30	0.5	5.80
			CO	McG	1.03	1.00	1.7	3.40
				p/a	0.90	2.10	1.7	0.03
			CH_4	SQ	2.02	3.00	2.3	9.70
				p/a	1.17	3.01	2.3	1.76
CaA	0.230	12796	CO_2	SQ	1.40	2.00	0.31	48.30
				p/a	4.47	3.01	0.31	4.75
			CO	McG	1.03	1.00	1.9	3.40
				p/a	1.47	2.54	1.5	0.50
			CH_4	SQ	2.02	3.00	1.6	9.70
				p/a	1.14	2.64	1.6	0.12
SKT-4	0.293	6731	CO_2	SQ	1.40	2.00	2.7	48.30
				p/a	1.43	1.69	2.7	1.83
			CO	McG	1.03	1.00	2.0	3.40
				p/a	1.28	1.83	2.0	0.35
			CH_4	K	1.52	2.00	1.7	0.50
				p/a	1.35	1.88	1.7	0.48

The results of comparing the minimum root mean square deviations achieved using the proposed approach (with the parameters presented in Table 4) with those based on literature data (selected from the sets of φ_i values in Table 6 at n_i =1, 2, 3) are shown in Tables 6 and 7.

An analysis of Tables 6 and 7 showed that, to ensure minimum deviations δ for different temperature intervals in the range of 293–333 K, different methods must be used to calculate φ_i (Keltsev [1], Sugden-Quayle and McGowan methods, as presented in the literature). However, there are no recommendations for selecting these methods.

Using the proposed approach yields significantly lower δ* values (no greater than 6.6 %) across the entire operating pressure range (up to 30×10^5 Pa) and temperature range (293–333 K).

4. Conclusion

The article proposes an approach for calculating equilibrium adsorption values of components in a hydrogen-containing gas mixture of CO_2, CO, and CH_4 at pressures up to 30×10^5 Pa and temperatures between 293 and 333 K, with an accuracy of no more than 6.6 % (in terms of standard deviation). Three experimental adsorption isotherms of the components of a hydrogen-containing gas mixture (CO_2, CO, and CH_4) on NaX, CaA, and SKT-4 are required, obtained at temperatures of 293, 313, and 333 K.

For all three adsorbents, the largest standard deviation values are observed for CO_2, which has a large isotherm inclination angle in the initial pressure range compared to CO, and CH_4on NaX, CaA, and SKT-4. Differences in affinity coefficient values for zeolites, as determined by the proposed approach versus literature data, are also observed for isotherms with a large slope angle in the initial pressure range (CO_2 on NaX and CaA, and CO on CaA).

It has been demonstrated that the equilibrium adsorption values of CO_2 and CO on NaX and SKT-4 can be calculated with a maximum deviation of no more than 10 % outside the temperature range of 293–333 K (at 253 K), for which the parameters of the Dubinin–Astakhov equation were calculated.

However, based on the analysis of the maximum deviations of the calculated and experimental isotherms, it was determined that using the proposed approach to calculate the equilibrium adsorption values of H_2 in the temperature range of 293–333 K on NaX, CaA, and SKT-4 does not provide sufficient accuracy for engineering calculations. Therefore, formal linear equilibrium dependencies were obtained based on experimental isotherms on NaX, CaA, and SKT-4 for the temperature range of 293–333 K.

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6. Conflict of interests

The authors declare no conflict of interests.

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Information about the authors / Информация об авторах

Dmitry S. Dvoretsky, D. Sc. (Eng.), Professor, Tambov State Technical University (TSTU), Tambov, Russian Federation; ORCID 0000-0002-4352-810X; e-mail: dvoretsky @yahoo.com

Stanislav I. Dvoretsky, D. Sc. (Eng.), Professor, TSTU, Tambov, Russian Federation; ORCID 0000-0002-7571-3748; e-mail: sdvoretsky@mail.tstu.ru

Evgeniy I. Akulinin, D. Sc. (Eng.), Associate Professor, TSTU, Tambov, Russian Federation; ORCID 0000-0003-0848-4380; e-mail: akulinin-2006@yandex.ru

Evgeny N. Tugolukov, D. Sc. (Eng.), Professor, TSTU, Tambov, Russian Federation; ORCID 0000-0003-1766-3786; e-mail: tugolukov.en@mail.ru

Gleb I. Varnikov, Student, TSTU, Tambov, Russian Federation; e-mail: glebvarnikov@gmail.com

Vladimir B. Usachev, Head of JSC Research Institute of Scientific Production Association Luch, Protvino branch, Protvino, Russian Federation; e-mail: npo@sialuch.ru

Дворецкий Дмитрий Станиславович, доктор технических наук, профессор, Тамбовский государственный технический университет (ТГТУ), Тамбов, Российская Федерация; ORCID 0000-0002-4352-810X; e-mail: dvoretsky@yahoo.com

Дворецкий Станислав Иванович, доктор технических наук, профессор, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0002-7571-3748; e-mail: sdvoretsky@mail.tstu.ru.

Акулинин Евгений Игоревич, доктор технических наук, доцент, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0003-0848-4380; e-mail: akulinin-2006@yandex.ru

Туголуков Евгений Николаевич, доктор технических наук, профессор, ТГТУ, Тамбов, Российская Федерация; ORCID 0000-0003-1766-3786; e-mail: tugolukov.en@mail.ru

Варников Глеб Игоревич, студент, ТГТУ, Тамбов, Российская Федерация; e-mail: glebvarnikov@ gmail.com

Усачев Владимир Борисович, директор протвинского филиала АО «НИИ НПО «Луч», Протвино, Российская Федерация, e-mail: npo@sialuch.ru

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