

## Thermodynamics of gas mixtures in nanoporous materials: Extension to non-ideal systems at high pressures

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**ABSTRACT** In this work, we developed a phenomenological approach to describe the equilibrium adsorption of nonideal gas mixtures in nanoporous adsorbents over a wide pressure range. The key point of the developed approach is an observation that the Gibbs free energy of a gas mixture is close to its ideal term. This feature, being more general than the empirical Raoult's law in the ideal adsorbed solution theory (IAST), was combined with the distribution of elements of the adsorption volume (EAV) of the porous material over potentials in the spirit of Polanyi's theory. We applied this approach to the adsorption of individual and binary gas mixtures of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> on an activated carbon in a wide pressure range up to 13 MPa. The approach provides high accuracy in predicting the adsorption of gas mixtures based on individual adsorption isotherms and obeys the Gibbs-Duhem equation, which confirms its thermodynamic consistency.

**KEYWORDS** high-pressure adsorption, supercritical gases, nanoporous carbons, mixture adsorption, adsorbed phase thermodynamics, equation of state.

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### 1. Introduction

Multicomponent adsorption of supercritical gas mixtures by nanoporous materials, in particular activated carbons, is widely used in gas separation and purification processes. In some cases, it is necessary to separate gases with similar physical properties, for example, nitrogen and methane, to reduce methane emissions into the environment or to purify natural gas from nitrogen during its liquefaction. In other cases, it is necessary to separate gases that have significantly different physical properties, such as carbon dioxide, methane, and nitrogen, which are part of the biogas. Biogas is a promising source of methane as a “green” fuel. Ensuring the efficiency of gas separation processes by adsorption requires reliable theoretical approaches for predicting multicomponent adsorption equilibrium. The theory of ideal adsorbed solution (IAST) of Myers and Prausnitz [1] has received the greatest application in describing multicomponent adsorption of gases. The ideality of the adsorbed solution essentially means the ideality of the bulk phase, which allowed the authors to resort to Raoult's law as an analog in relation to the adsorption system. This imposes obvious restrictions on the use of IAST when modeling the binary adsorption of CO<sub>2</sub>–CH<sub>4</sub> or CO<sub>2</sub>–N<sub>2</sub> mixtures by activated carbons at high pressures, reaching 1 [2], 2.5 [3, 4], 6 [5], and even 14 MPa in some studies [6–8]. It has been established [2] that the accuracy of the IAST prediction of phase diagrams at constant pressure in the gas phase increases with increasing pressure from 0.1 to 1 MPa, while the deviation between predicted and experimental values decreases from 30 to 5.5%. It was also observed [3] that IAST provides a good prediction of the CO<sub>2</sub>–CH<sub>4</sub> mixture over a whole pressure range from 0 to 3 MPa. However, later, the same authors [4] pointed out that the same system is well described by IAST only in the range of 0–1.5 MPa. Additional contradictions arise due to the use of extensions of the Langmuir and Sips equations for multicomponent adsorption [2, 5, 7, 8], although it is known that such extensions are thermodynamically valid only for the same limiting values of individual adsorption of mixture components [9]. This requirement is usually ignored. To overcome some shortcomings of the original IAST, some improvements were made to it. Thus, the heterogeneity of the adsorbent was introduced into the theory [10], suggesting that adsorption occurs independently on each surface area with the same energy. The authors called this modification HIAST. In a number of cases, this provided better agreement with experimental data. A more extended approach called the multispace adsorption model (MSAM) was presented by Jensen et al. [11]. The authors proceeded from the idea of the non-uniformity of the adsorption phase and introduced two spaces in the adsorption volume. In the first space, presumably near the pore walls, adsorption occurs independently, while in the second, the amount of the adsorbed mixture and its composition depend on those in the first space. As in the previous case, the IAST was used in combination with the energy distribution of elements of the adsorption volume,

determined from individual adsorption isotherms. The authors successfully applied their approach to the adsorption of a methane-ethane mixture on an activated carbon at bulk pressures up to 30 bar. A similar idea was developed in the MPD (Myers-Prausnitz-Dubinin) model [12], where the Dubinin-Radushkevitch (DR) equation, extended to the supercritical region [13], was combined with the IAST. The authors applied their model to the adsorption of a CO<sub>2</sub>-CH<sub>4</sub> mixture on a commercial activated carbon at constant pressures (0.1 and 1 MPa) and temperatures of 273 and 298 K and demonstrated excellent agreement between the calculated phase diagrams and experimental data. One more group of works rely on equations of state (EOS) extended to mixtures using arbitrary chosen combining rules for various parameters [6, 14–16]. This option requires reliable theoretical approaches for predicting multicomponent adsorption equilibrium.

Apparently, the most coherent approach is described in [17, 18], which is close to our model used in this study. The theoretical basis of the approach, called the Multicomponent Potential Theory of Adsorption (MPTA), follows from Polanyi's idea [19] of an adsorption potential distributed over the adsorption space, which contributes to the chemical potential in the adsorbed phase and, consequently, shifts the vapor-liquid equilibrium towards lower pressure values. The second assumption in the MPTA, taken from Polanyi's theory, was that a gas under the influence of an adsorption field behaves in accordance with its normal equation of state. The potential distribution, which can be obtained by analyzing adsorption isotherms of pure components, was used by the authors in the form of the DR equation extended to the supercritical region. The use of some additional assumptions to extend the equation of state to mixtures made it possible to describe with acceptable accuracy the adsorption of binary gas mixtures under high pressure on activated carbons and MOF.

This work is also based on Polanyi's idea of independent adsorption in elements of adsorption volume distributed over potential. We used this approach previously for determining the potential distribution function of an activated carbon [20] from the individual adsorption isotherms. Further, we extended this approach to the adsorption of gas mixtures using the Bender EOS and a set of combining rules for several EOS parameters [16]. Here we use a more general and rigorous thermodynamic method for extending EOS to gas mixtures, reminiscent of the idea behind IAST. In the present study, we apply the approach only to supercritical systems under high-pressure conditions, which poses a significant challenge for accurately describing mixture adsorption.

## 2. Model and thermodynamics

We rely on a simplified model of the elements of adsorption volume (EAV) [16, 20] distributed over the potential. Each element of the adsorption volume is not necessarily associated with a specific micro- or mesopore of the adsorbent. An element that is characterized by a certain potential,  $u$ , can simultaneously belong to several pores of different sizes or parts of them, if the potential inside them is not uniform. Thus, the distribution of EAVs of potential is an indirect characteristic of the porous structure of the adsorbent, not directly related to the pore size distribution. The absence of a specific physical image of the structure of active carbons in the proposed model is to some extent justified by their actual complexity, but nevertheless allows us to apply thermodynamics to a quantitative description of the relationship between the adsorption of individual components and their mixtures.

### 2.1. Individual adsorption

Let  $f(u)$  be the distribution function of EAVs on the potential  $u$ , so that the integral of  $f$  is the pore volume of the adsorbent,  $W_0$ , i.e.,

$$W_0 = \int_{u_{\min}}^{u_{\max}} f(u) du. \quad (1)$$

Then the amount adsorbed of an individual component is:

$$a = \int_{u_{\min}}^{u_{\max}} \rho(T, \mu - \beta u) f(u) du. \quad (2)$$

Here  $\rho$  is the density of the adsorbed phase that depends on temperature,  $T$  and the intrinsic chemical potential  $\mu' = \mu - \beta u$ , where  $\mu$  is the chemical potential in the bulk phase and  $\beta$  is the affinity coefficient of the component.

The density of the adsorbed phase can be determined using any equation of state. In this study we relied on Bender EOS for the pressure as a function of  $T$  and  $\rho$  [21]:

$$p = \rho RT + T \sum_{k=1}^5 B_k \rho^{k+1} + T(B_6 + B_7 \rho^2) \rho^3 \exp(-a_{20} \rho^2). \quad (3)$$

Here  $R$  is the gas constant; parameters  $B_k$  ( $k = 1, \dots, 7$ ) are functions of temperature. In total, twenty EOS constants  $a_k$  ( $k = 1, \dots, 20$ ) have been determined for many gases. The chemical potential can easily be obtained in an analytical form by integration the relation  $d\mu = \rho^{-1} dp$ :

$$\mu = RT \ln \rho + \mu^r. \quad (4)$$

The first and second terms in the right side of Eq. (4) are the ideal and residual parts of the chemical potential, respectively. The standard chemical potential  $\mu^\circ(T)$  is omitted because it cancels out in all balance ratios. For the residual chemical potential we have:

$$\mu^r = T \sum_{k=1}^5 B_k \frac{k+1}{k} \rho^k + T \left[ (B_6 + B_7 \rho^2) \left( \rho^2 - \frac{1}{2a_{20}} \right) - B_7 \frac{1}{2a_{20}^2} \right] \exp(-a_{20} \rho^2). \quad (5)$$

For a given chemical potential  $\mu$  in the bulk phase, the density in the EAV with potential  $u$  is the root of the following equation:

$$RT \ln \rho + \mu^r(T, \rho) = \mu - \beta u. \quad (6)$$

Having an adsorption isotherm, it is possible to determine the distribution of EAVs over potential  $u$  for a specific adsorbent.

## 2.2. Binary mixture adsorption

As shown in [22], the entropy of mixing of a supercritical Ar-Kr mixture is very close to the ideal mixing entropy even at high pressures (at least up to 200 bar), when the densities of the gas components are comparable to the densities of liquid phases at subcritical temperatures, i.e., the supercritical individual gases were not ideal. It was also shown, that the enthalpy of mixing of the same Ar-Kr mixture is weakly convex function of composition and does not exceed 0.11 kJ/mol. This means that the Gibbs free energy of mixing is also close to the corresponding ideal value, i.e.,

$$G = n_1 \mu_1 + n_2 \mu_2 = n_1 \mu_1^\circ + n_2 \mu_2^\circ + RT (n_1 \ln x_1 + n_2 \ln x_2). \quad (7)$$

Here  $n_j$ ,  $\mu_j$  are number of molecules of the component  $j$  ( $j = 1, 2$ ) and its chemical potential at a given pressure  $p$ ;  $\mu_j^\circ$  is the chemical potential of the individual component  $j$  at the same pressure  $p$ ;  $x_1$ ,  $x_2$  are molar fractions of component 1 and 2, respectively. From Eq. (7) it follows that

$$\mu_j^\circ = \mu_j - RT \ln x_j, \quad j = 1, 2. \quad (8)$$

Given the potential  $u$  in a particular EAV, Eqs. (8) can be rearranged to the following form:

$$\mu_j^\circ = \mu_j - \beta_j u - RT \ln x_j, \quad j = 1, 2. \quad (9)$$

Here the apostrophe means that the chemical potential is taken in the adsorbed phase (EAV) at the pressure  $\Pi$  not equal to the bulk pressure  $p$ . We also take into account the different affinity coefficients of the components relative to the potential  $u$ . The density  $\rho_j^\circ$  of component  $j$  corresponds to the chemical potential  $\mu_j^\circ$  when this component is individual at the same temperature and pressure  $\Pi$  as in the mixture, while

$$\frac{\rho_1}{\rho_1^\circ} + \frac{\rho_2}{\rho_2^\circ} = 1. \quad (10)$$

It is important to note that Eq. (10) is a consequence of the Gibbs-Duhem equation and therefore has a general form regardless whether the system and individual components are ideal or not.

The system of Eqs. (8) and (10) is sufficient to determine the densities in EAV with the potential  $u$ . The algorithm is as follows.

(1) Having a pair of chemical potentials  $\mu_1$  and  $\mu_2$  in the bulk phase, eliminating  $x_1$  and  $x_2 (= 1 - x_1)$  from Eqs. (9) leads to the following relationship:

$$\exp\left(\frac{\mu_1 - \beta_1 u - \mu_1^\circ}{RT}\right) + \exp\left(\frac{\mu_2 - \beta_2 u - \mu_2^\circ}{RT}\right) = 1. \quad (11)$$

The root of this equation is pressure  $\Pi$ , which immediately gives values of  $\mu_1^\circ$ ,  $\mu_2^\circ$ ,  $\rho_1^\circ$ , and  $\rho_2^\circ$ .

(2) Knowing  $\mu_1^\circ$ ,  $\mu_2^\circ$ , the composition of the mixture can be determined using any of equations (9).

(3) Once the composition is known, the total density in the EAV is

$$\rho_1 + \rho_2 = 1 / [x_1 / \rho_1^\circ + x_2 / \rho_2^\circ]. \quad (12)$$

The above equation follows from Eq. (10).

(4) Densities in the EAV are defined as

$$\rho_j = x_j (\rho_1 + \rho_2), \quad j = 1, 2. \quad (13)$$

(5) Finally, the amount adsorbed of the component  $j$  is determined as

$$a_j = \int_{u_{\min}}^{u_{\max}} \rho_j(T, \mu_1, \mu_2, u) f(u) du, \quad j = 1, 2. \quad (14)$$

### 2.3. The case of an ideal bulk phase

First, let us consider the case when adsorption occurs in a thin layer on a homogeneous surface. Then the composition of the adsorbed phase does not change over its volume at given chemical potentials  $\mu_1$  and  $\mu_2$ , and the values  $\mu_1^\circ$ ,  $\mu_2^\circ$  in Eqs. (8) correspond to chemical potential of individual gases in the bulk phase at the same pressure  $\Pi$  in the adsorption phase. If, in addition, the bulk phase is ideal, then from Eqs. (8) we have:

$$p_j = x_j p_j^\circ, \quad j = 1, 2. \quad (15)$$

This is Raoult's law adopted for the adsorbed phase in the ideal adsorbed solution theory (IAST) [1]. The values  $p_1^\circ$ ,  $p_2^\circ$  are bulk pressures of individual components when the corresponding amounts adsorbed  $a_1^\circ$ ,  $a_2^\circ$  are at the same pressure  $\Pi$  in the adsorption phase. Since the density of each component is uniformly distributed throughout the adsorbed phase, the following relationship can be written instead of Eq. (10):

$$\frac{a_1}{a_1^\circ} + \frac{a_2}{a_2^\circ} = 1. \quad (16)$$

Interestingly, Eq. (16) is very general and is also valid in the case of non-uniform adsorption phase, but values  $a_1^\circ$ ,  $a_2^\circ$  are determined at the same average adsorbed phase pressure  $\bar{\Pi}$  that can be easily calculated from individual adsorption isotherms.

Thus, IAST is a special case of a more general approach considered in this study. The advantage of IAST is that the use of EOS is not required. Instead, one can use a specific form of adsorption isotherm for each component, which is much simpler. On the other hand, the disadvantage is the limitation to the region of low pressures of the mixture, when the bulk phase is ideal.

### 2.4. Non-ideality of the adsorbed phase

In a more general case, it is reasonable to account for the non-ideality of the adsorption phase, which may be associated with the effect of the pore walls on the confined gas mixture. All existing equations for activity coefficients are derived under the condition of constant pressure. In the limiting case of very low pressures, the gas mixture must be ideal. For this reason, in this work we relied on the simplest Margules equation, which in our case is included in Eqs. (9) as follows:

$$\mu_j^\circ = \mu_j - \beta_j u - RT [\ln x_j + \alpha \Pi (1 - x_j)^2], \quad j = 1, 2. \quad (17)$$

The only constant  $\alpha$  can be determined by the least-squares fitting procedure.

## 3. Results and discussion

### 3.1. Individual isotherms

In this section, we consider the adsorption isotherms of pure gases by activated carbon by utilizing the model of elements of adsorption volume distributed by potential energy. A preliminary analysis of the results previously obtained in the framework of this model using the regularization method ([16, 20]) showed that of the EAV distribution is well approximated by the following simple function:

$$f(u) = b_1 \exp(-b_2 u + b_3 u^2). \quad (18)$$

It is assumed that this equation is written for the reference component (in our case  $\text{CO}_2$ ) and the three coefficients are the same for any other gas, but its difference in the potential of interaction with EAV is taken into account by the affinity coefficient  $\beta$ . This means that describing of, for example, three isotherms of pure components requires the determination of five coefficients, including an additional two affinity coefficients for gases other than the reference. Joint processing of several adsorption isotherms reduces the total number of coefficients and, thereby, increases the reliability of determining the EAS distribution function by reducing their interrelation. An additional coefficient is the upper limit of the potential  $u_{max}$  for a specific activated carbon and the lower limit  $u_{min}$  can formally be taken equal to  $-\infty$ , since the exponential function decreases sharply with decreasing potential, starting from a certain value.

Figure 1a shows the isotherm of excess adsorption of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  on activated carbon Filtrasorb-400 at 318.2 K from data published by M. Sudibandryo et.al. [6]. This activated carbon is manufactured by Calgon Carbon Corporation and is specified by the manufacturer to have an effective pore size distribution ranging from 0.55 to 0.75 nm (average 0.64 nm).

It is known that the adsorption excess can be directly determined by experiment, whereas absolute values of amount adsorbed require additional assumptions about the volume of the adsorbed phase. For this reason, we further compare theoretical results only with excess adsorption in the case of both individual and binary experimental adsorption data. The excess adsorption was calculated using the following equation:

$$a = \int_{u_{min}}^{u_{max}} [\rho(T, \mu - \beta u) - \rho(T, \mu)] f(u) du. \quad (19)$$

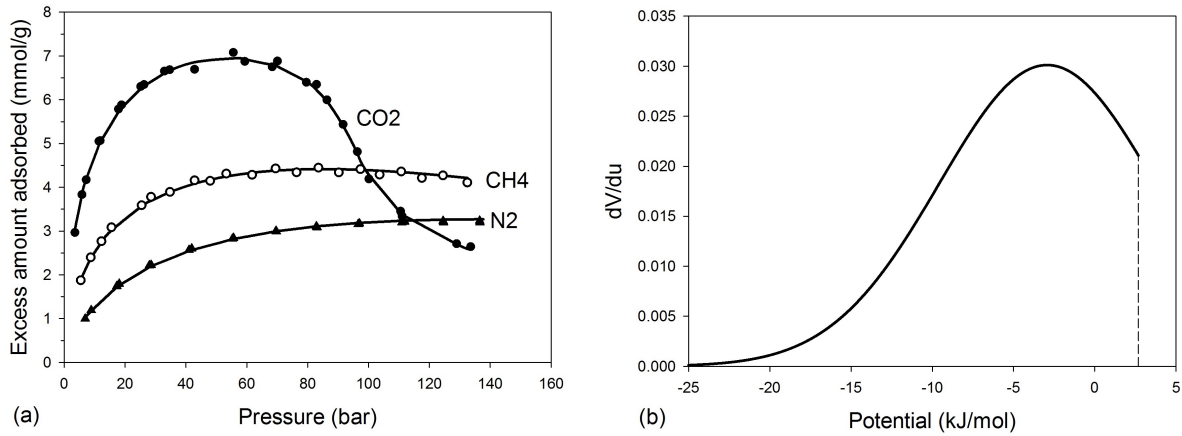


FIG. 1. (a) Calculated excess adsorption isotherms of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  on activated carbon Filtrasorb-400 (lines) vs experimental data (symbols) [6] at 318.2 K. Lines are calculations using distribution (17) and the Bender's EOS. (b) Distribution of EAVs over the potential

The second term in square brackets is the gas density in the bulk phase. The lower limit  $u_{min}$  was taken to be  $-35$  kJ/mol, when the function  $f(u_{min})$  becomes negligible.

The least squares coefficients for the EAVs distribution function were 0.02734, 0.06620, and 0.01131 for  $b_1$ ,  $b_2$ , and  $b_3$ , respectively. The resulting affinity coefficients  $\beta_2$ ,  $\beta_3$  were 0.9886, and 0.7694 for methane and nitrogen, respectively, under the assumption that  $\beta_1 = 1$  for carbon dioxide. The upper limit  $u_{max}$  turned out to be 2.694 kJ/mol. The total pore volume  $W_0$  calculated by Eq. (1) is  $0.402 \text{ cm}^3/\text{g}$ . The EAV distribution over the potential is shown in Fig. 1b. In fact, it is part of a Gaussian or normal function with a mean expectation  $u_0$  of  $-2.925$  kJ/mol and a standard deviation  $\sigma$  of 4.7 kJ/mol.

### 3.2. Binary isotherms

Binary excess adsorption isotherms are calculated according to the following algorithm.

(I) At a given temperature and bulk pressure  $p$ , individual chemical potentials  $\mu_1^\circ$ ,  $\mu_2^\circ$  and densities  $\rho_1^\circ$ ,  $\rho_2^\circ$  are determined with the EOS. Then, for known fractional composition  $y_1$ ,  $y_2 = 1 - y_1$  chemical potentials  $\mu_1$ ,  $\mu_2$  are determined using the following relationships:

$$\mu_j = \mu_j^\circ + RT [\ln y_j + \alpha p(1 - y_j)^2], \quad j = 1, 2. \quad (20)$$

The actual densities  $\rho_1^b$  and  $\rho_2^b$  in the bulk phase can be further calculated using the equation, which is a combination of Eqs. (12) and (13):

$$\rho_j = y_j / [y_1 / \rho_1^\circ + y_2 / \rho_2^\circ], \quad j = 1, 2. \quad (21)$$

(II) For a given potential  $u$  in the selected EAV, the local chemical potentials are  $\mu_1 - \beta_1 u$  and  $\mu_2 - \beta_2 u$  for the first and second components, respectively. To determine the composition and pressure at given chemical potentials in the EAV, it is necessary to solve the following system:

$$\left. \begin{aligned} \mu_1^\circ &= \mu_1 - \beta_1 u - RT [\ln x_1 + \alpha \Pi x_2^2], \\ \mu_2^\circ &= \mu_2 - \beta_2 u - RT [\ln x_2 + \alpha \Pi x_1^2], \end{aligned} \right\} \quad (22)$$

where  $\mu_1^\circ$ ,  $\mu_2^\circ$  are functions of the same pressure  $\Pi$  for corresponding pure components.

The root of the system of equations (22) is  $\Pi$  and  $x_1$  (or  $x_2$ , which does not matter). At the same time, this gives densities  $\rho_1^\circ$ ,  $\rho_2^\circ$  of individual components corresponding to the pressure  $\Pi$ . The actual densities in the EAV can then be calculated with relations, similar to those in Eqs. (21):

$$\rho_j = x_j / [x_1 / \rho_1^\circ + x_2 / \rho_2^\circ], \quad j = 1, 2. \quad (23)$$

(III) At the final stage, the adsorbed amounts of the mixture components are determined by integration over all elements of adsorption volume, distributed over potential  $u$ :

$$a_j = \int_{u_{min}}^{u_{max}} [\rho_j(T, \mu_1', \mu_2') - \rho_j^b(T, \mu_1, \mu_2)] f(u) du, \quad j = 1, 2. \quad (24)$$

Isotherms of carbon dioxide and methane on Filtrasorb-400 from  $\text{CO}_2$ - $\text{CH}_4$  mixture are presented in Fig. 2.

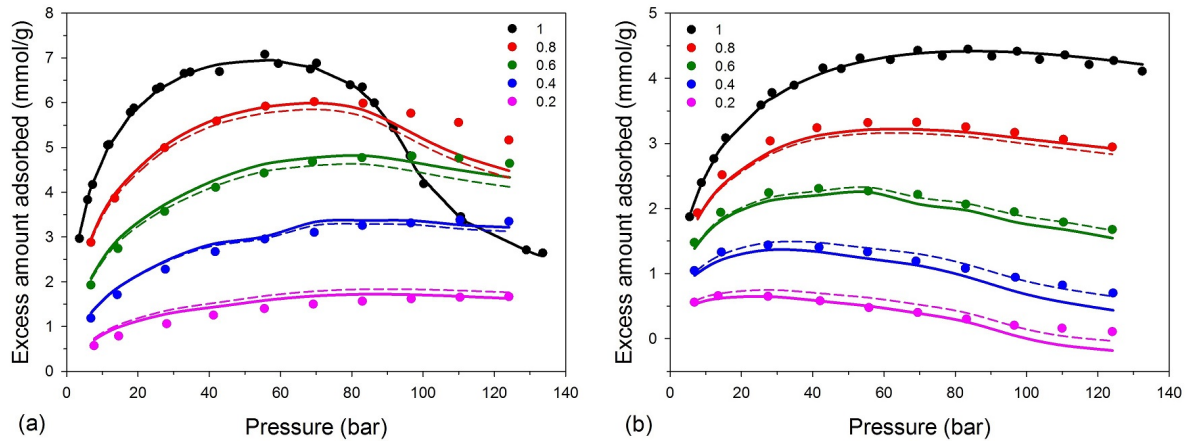


FIG. 2. Comparison of the calculated and experimental excess adsorption of  $\text{CO}_2$  and  $\text{CH}_4$  on activated carbon Filtrasorb-400 from a  $\text{CO}_2$ – $\text{CH}_4$  gas mixture at 318.2 K. The circles represent the experimental data from Ref. 6, and the lines represent calculations using the proposed method, accounting for the distribution (17) and a coefficient  $\alpha$  of  $0.000174 \text{ bar}^{-1}$  in Eqs. (19) and (21). The dashed lines correspond to the ideal mixing Gibbs free energy at  $\alpha = 0$ . The numbers at the curves indicate the molar fraction of  $\text{CO}_2$  (a) and  $\text{CH}_4$  (b) in the gas phase, so the black circles and lines indicate adsorption of pure  $\text{CO}_2$  (a) and  $\text{CH}_4$  (b), respectively

As seen in Fig. 2, the agreement between experimental data and calculations is quite good despite we used the only adjusting parameter  $\alpha$ . However, even with a zero value of  $\alpha$ , i.e. in the absence of adjusting parameters, the description of experimental data remains acceptable.

In a similar way, experimental adsorption isotherms for binary systems  $\text{CO}_2$ – $\text{N}_2$  and  $\text{CH}_4$ – $\text{N}_2$  can be analyzed. Corresponding results are presented in Figs. 3,4.

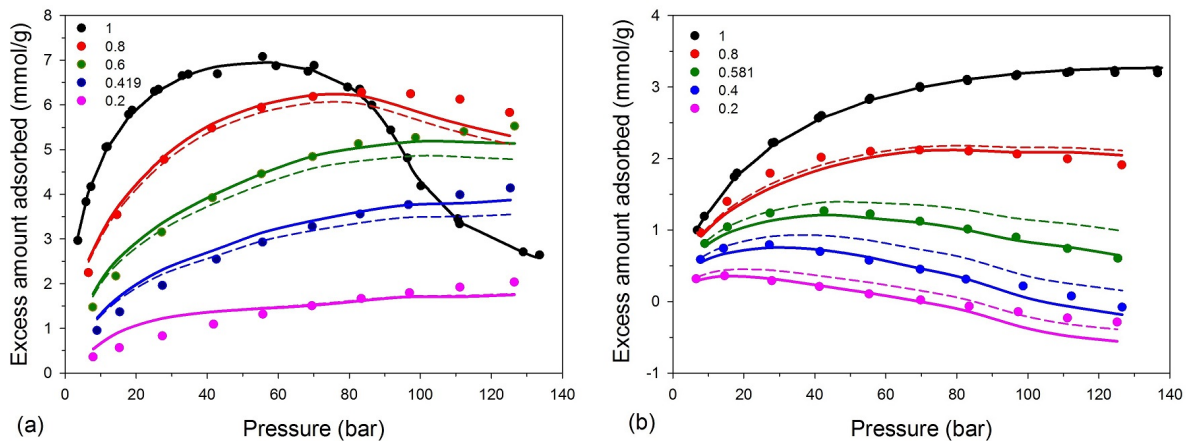


FIG. 3. Experimental [6] and calculated excess adsorption isotherms of  $\text{CO}_2$  and  $\text{N}_2$  on activated carbon Filtrasorb-400 from  $\text{CO}_2$ – $\text{N}_2$  mixture at 318.2 K. Coefficient  $\alpha$  is  $0.000469 \text{ bar}^{-1}$  (solid lines) and 0 (dashed lines). The remaining conditions are the same as in Fig. 2

As can be seen from Figs. 2–4, in all examples of binary mixtures the concept works very reliably over a wide range of pressures in the bulk phase.

### 3.3. Adsorbed phase pressure

The pressure depends on the potential  $u$  in a specific element of the adsorbed phase and, for given chemical potentials of the components of a binary mixture, is the root of Eqs. (22) along with the fractional composition. The average pressure in the adsorption phase is determined by the following equation:

$$\bar{\Pi} = W_0^{-1} \int_{u_{\min}}^{u_{\max}} f(u) \Pi du. \quad (25)$$

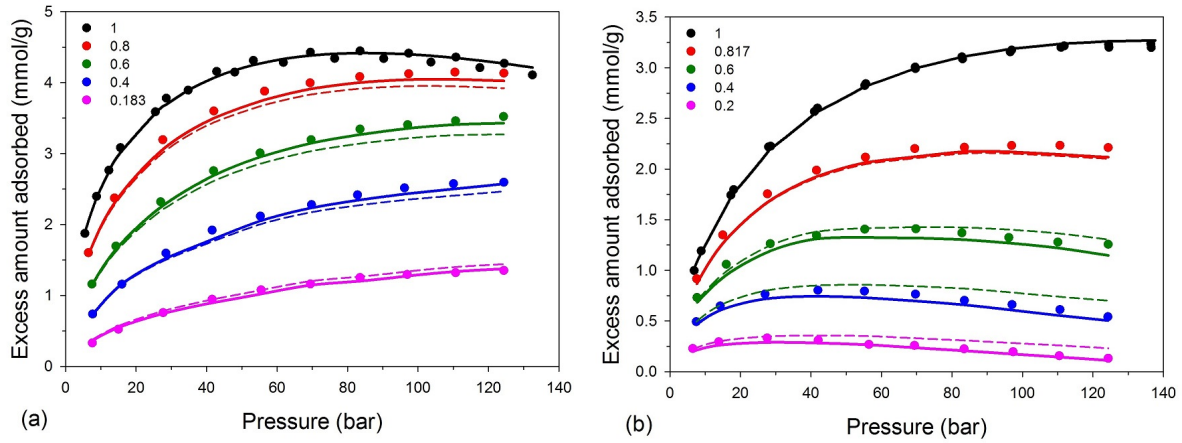


FIG. 4. Experimental [6] and calculated excess adsorption isotherms of CH<sub>4</sub> and N<sub>2</sub> on activated carbon Filtrasorb-400 from CH<sub>4</sub>-N<sub>2</sub> mixture at 318.2 K. Coefficient  $\alpha$  is 0.000292 bar<sup>-1</sup> (solid lines) and 0 (dashed lines). The remaining conditions are the same as in Fig. 2

Fig. 5 presents the average pressure in the adsorption phase as a function of the bulk pressure for a CO<sub>2</sub>-CH<sub>4</sub> mixture at various compositions in the bulk phase.

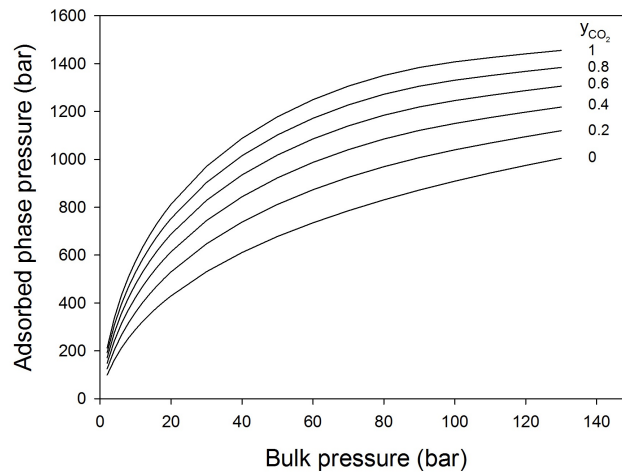


FIG. 5. Average pressure in the adsorbed CO<sub>2</sub>-CH<sub>4</sub> mixture on activated carbon Filtrasorb-400 at 318.2 K. The numbers in the legend are mole fraction of carbon dioxide in the bulk phase

The average pressure reaches 1500 bar, which is an order of magnitude higher than the bulk pressure. Taking into account the Gibbs-Duhem equation for a given potential  $u$  in the EAV,

$$d\Pi = \rho_1 d\mu_1 + \rho_2 d\mu_2, \tag{26}$$

we have:

$$W_0 d\bar{\Pi} = \int_{u_{\min}}^{u_{\max}} f(u) [\rho_1 d\mu_1 + \rho_2 d\mu_2] du.$$

In equivalent form the above equation can be rewritten as

$$W_0 d\bar{\Pi} = a_1 d\mu_1 + a_2 d\mu_2. \tag{27}$$

This means that the Gibbs-Duhem equation in the form of Eq (27) is satisfied in the proposed method.

The Gibbs-Duhem equation can also be written for individual components, i.e.,

$$W_0 d\bar{\Pi} = a_j^\circ(\bar{\Pi}) d\mu_j, \quad j = 1, 2. \tag{28}$$

Combining Eqs. (27) and (28), we again obtain Eq. (16), where  $a_1^\circ, a_2^\circ$  are amounts of individual adsorption at the same average adsorbed phase pressure.



### 3.4. Thermodynamic consistency of experimental data

As mentioned earlier, excess quantities can only be obtained experimentally, so it is crucial to create an analog of the Gibbs-Duhem equation for excess functions. This can be done by subtracting from Eq. (27) a similar equation written for the bulk phase:

$$W_0 dp = W_0 \rho_1^b d\mu_1 + W_0 \rho_1^b d\mu_2.$$

This gives

$$W_0 d(\bar{\Pi} - p) = a_1^{ex} d\mu_1 + a_2^{ex} d\mu_2. \quad (29)$$

The variable  $(\bar{\Pi} - p)$  can be called excess pressure  $\bar{\Pi}^{ex}$ , which at a given temperature can be considered as a function of chemical potentials  $\mu_1$  and  $\mu_2$ . Since the chemical potential tends to  $-\infty$  at zero density, it is more convenient to use  $v_1 = \exp[\mu_1/(RT)]$  and  $v_2 = \exp[\mu_2/(RT)]$  as independent parameters. Let the function  $W_0 \bar{\Pi}^{ex}$  be written as a polynomial:

$$W_0 \bar{\Pi}^{ex} = \sum_{j=0}^n \sum_{k=0}^n b_{jk} v_1^j v_2^k \quad (30)$$

Then

$$\left. \begin{aligned} a_1^{ex} &= W_0 \frac{\partial \bar{\Pi}^{ex}}{\partial \mu_1} = \frac{1}{RT} \sum_{j=0}^n \sum_{k=0}^n j b_{jk} v_1^j v_2^k, \\ a_2^{ex} &= W_0 \frac{\partial \bar{\Pi}^{ex}}{\partial \mu_2} = \frac{1}{RT} \sum_{j=0}^n \sum_{k=0}^n k b_{jk} v_1^j v_2^k. \end{aligned} \right\} \quad (31)$$

The advantage of system (31) is that to calculate the excess amount of adsorbed both the first and second components, the same set of coefficients  $b_{jk}$  is used, and the thermodynamic consistency of calculations is guaranteed. The coefficients  $b_{jk}$  are determined by the standard least-squares technique using both mixture and individual experimental adsorption isotherms at a condition that the coefficient  $b_{00}$  is zero. The thermodynamic consistency of experimental data is assessed by small variations between the experimental values of excess adsorption and those calculated using equations (31).

Figure 6 presents the results of a regression analysis of experimental data on the adsorption of a  $\text{CO}_2$ - $\text{CH}_4$  mixture on Filtrasorb-400 activated carbon. The upper summation limits  $n$  in Eqs. (31) were taken to be 4.

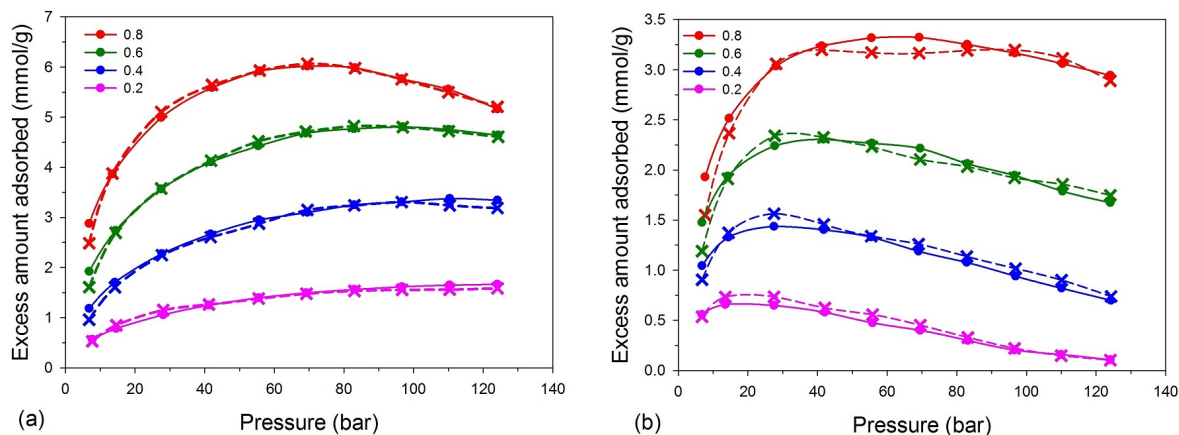


FIG. 6. Isotherms of excess adsorption of  $\text{CO}_2$  (a) and  $\text{CH}_4$  (b) from  $\text{CO}_2$ - $\text{CH}_4$  gas mixture on activated carbon Filtrasorb-400 [6] at 318.2 K. Circles are experimental data. Solid lines indicate the results of regression analysis using Eqs. (30). The numbers at the symbols represent the mole fractions of carbon dioxide and methane, respectively, in the feed gas

Lines in Fig. 6 show smoothed experimental adsorption excess values (circles) as required by the Gibbs-Duhem equation. Relatively small deviations between experimental and corrected amounts of adsorption confirm the thermodynamic consistency of experimental data. This is quite expected for supercritical fluid mixtures, but in case of adsorption of vapor mixtures it is not obvious, since equilibrium during the mixing process in the condensed liquid-like adsorbed phase occurs noticeably more slowly. In the latter case, the confirmation of thermodynamic consistency of experimental data should precede their further analysis.



#### 4. Conclusion

An improved method for predicting the adsorption of a gas mixture using adsorption isotherms of pure gases is proposed. The idea behind the approach is that the Gibbs free energy of mixing is close to its ideal value. This can be formulated as the ideal mixing of non-ideal gases in the adsorbed phase, the elements of which are distributed over the potential. Using the equation of state of the individual components, this condition allows for the determination of the pressure and composition of the mixture in the adsorbed phase for given chemical potentials. We chose Bender's equation of state for this purpose, but any other suitable equation of state can be used as well. Therefore, the proposed approach is fundamentally different from the ideal adsorbed solution theory and does not rely on the Raoult's law in the adsorbed phase. The approach has been tested on a well-studied CO<sub>2</sub>-CH<sub>4</sub>- activated carbon system. All previous methods based on the IAST (see references 2-4, 8, and 12, for example) can more or less quantitatively describe the system under bulk pressures up to 1–1.3 MPa. Contrary to this, our approach exceeds the pressure range by at least one order of magnitude using directly measured excess experimental values as input, which has been validated by its application to experimental data from reference 6. The possibility of increasing the descriptive ability of the method is also provided by using an additional adjustable parameter.

A general method was also proposed for checking the thermodynamic consistency of experimental data on the adsorption of gas mixtures.

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