

A Simplified Integral Equation for Adsorption of Gas Mixtures on Heterogeneous Surfaces

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Summary. The multiple integral representing the overall isotherm for adsorption of gas mixtures on heterogeneous surfaces is transformed to a single integral, which is promising for predicting the mixed-gas adsorption by means of single-gas adsorption parameters. This transformation is possible when the adsorption energies of components for various adsorption sites show a certain type of correlation.

Keywords. Mixed-gas adsorption; Simplified integral equation for adsorption; Prediction of multi-component adsorption.

Eine vereinfachte Integralgleichung für die Adsorption von Gasmischungen auf heterogenen Oberflächen

Zusammenfassung. Das multiple Integral, das die Adsorption von Gasmischungen auf heterogenen Oberflächen darstellt, wurde zu einem einfachen Integral transformiert, das zur Voraussage der Adsorption von Gasgemischen mittels der Einzelgas-Adsorptionsparameter geeignet sein sollte. Diese Transformation ist dann möglich, wenn die Adsorptionsenergien der Komponenten einem bestimmten Korrelationstyp angehören.

The role of surface heterogeneity in gas adsorption was studied by many authors (see reviews [1–6] and references therein). Although mixed-gas adsorption on heterogeneous surfaces was already considered in the 40s and 50s [7–11] a general integral equation for mixed-gas adsorption on energetically heterogeneous surfaces was proposed in 1975 [12, 13]. For a multicomponent gas mixture this equation has the following form [12, 13],

$$\theta_{i(n)t} = \int \dots \int_{\Delta E} \theta_{i(n)l}(\mathbf{p}, \mathbf{E}) \chi(\mathbf{E}) d\mathbf{E}, \quad i = 1, 2, \dots, n, \quad (1)$$

where $\theta_{i(n)t}$ and $\theta_{i(n)l}$ are the overall and local surface coverages for the “*i*”-th component of *n*-component mixture, $\mathbf{p} = (p_1, p_2, \dots, p_n)$ is the matrix of partial pressures, $\mathbf{E} = (E_1, E_2, \dots, E_n)$ is the matrix of reduced adsorption energies of all components, $\chi(\mathbf{E})$ is the *n*-dimensional distribution function of reduced adsorption energies and ΔE is the integration range.

In this paper, Eq. (1) is transformed to a simpler form, which seems to be promising for the prediction of mixed-gas adsorption on heterogeneous surfaces by means of the single-gas adsorption parameters. This equation makes it possible to formulate a prediction method for mixed-gas adsorption, which is more general in comparison to the previous ones [4].

For simplification of the further discussion, let us consider the adsorption of two-component gas mixture. In Fig. 1 the projections of two-dimensional distribution function $\chi(E_1, E_2)$ are presented in comparison to the distributions $\chi_i(E_i)$ ($i = 1, 2$) relating to the pure components. The distributions $\chi_i(E_i)$ for single components are connected with the two-dimensional distribution as follows:

$$\begin{aligned}\chi_1(E_1) &= \int_{\Delta E_2} \chi(E_1, E_2) dE_2, \\ \chi_2(E_2) &= \int_{\Delta E_1} \chi(E_1, E_2) dE_1.\end{aligned}\quad (2)$$

However, the two-dimensional distribution function $\chi(E_1, E_2)$ is used to define adsorption of binary gas mixtures on heterogeneous surfaces according to the following equation:

$$\theta_{i(2)t} = \int_{\Delta E_1} \int_{\Delta E_2} \theta_{i(2)t}(p_1, p_2, E_1, E_2) \chi(E_1, E_2) dE_1 dE_2, \quad i = 1, 2. \quad (3)$$

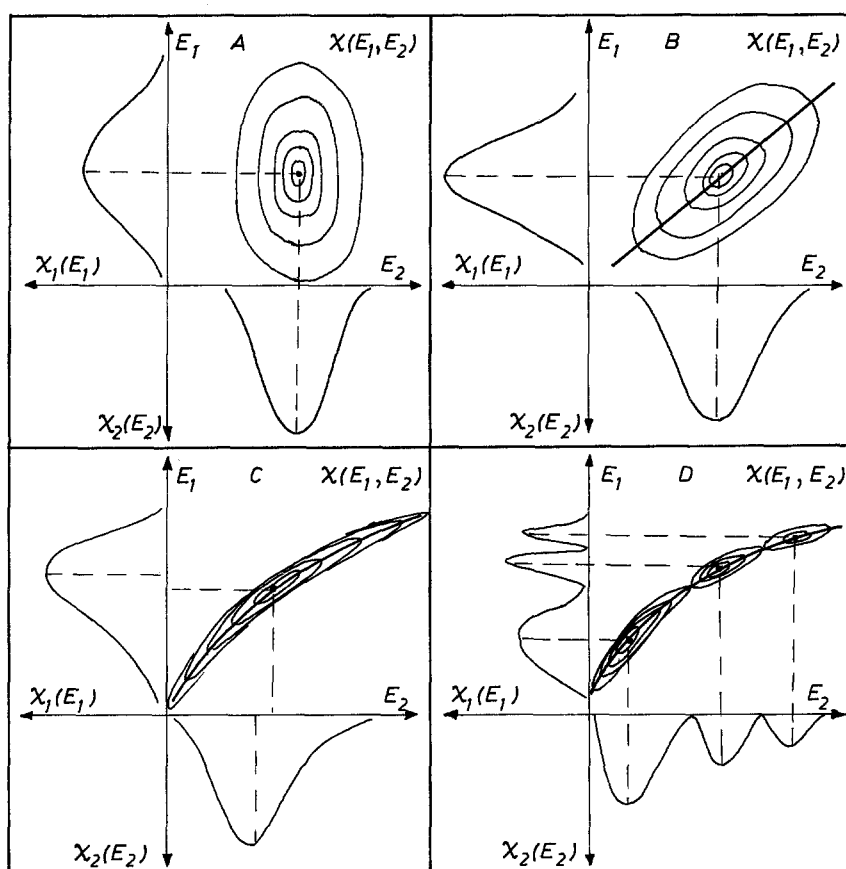


Fig. 1. Projections of model two-dimensional distribution functions $\chi(E_1, E_2)$ and the distributions $\chi_i(E_i)$ ($i = 1, 2$) relating to pure components. The graphs correspond to various values of correlation coefficients between adsorption energies: A: $r_{12} = 0$; B: $|r_{12}| \ll 1$; C, D: $|r_{12}| \approx 1$

In the part *A* of Fig. 1 an adsorption system showing a lack of correlation between adsorption energies of both components is considered (the correlation coefficient $r_{12} = 0$). Then, the two-dimensional energy distribution function may be treated as a product of two independent distributions relating to the pure components, i.e.,

$$\chi(E_1, E_2) = \chi_1(E_1)\chi_2(E_2). \quad (4)$$

Part *B* of Fig. 1 presents an adsorption system characterized by a poor correlation ($|r_{12}| \ll 1$) between adsorption energies of both components. However, in the parts *C* and *D* of Fig. 1 the cases of a strong correlation between adsorption energies of both components are shown ($|r_{12}| \approx 1$). Part *D* gives an example of a more complicated distribution function, which shows several peaks. Moreover, parts *C* and *D* of Fig. 1 explain the possibility of existence of a good correlation between adsorption energies in a multicomponent adsorption system for which the single-component systems are characterized by the distribution functions of different shapes. In the case of adsorption systems showing a good correlation between adsorption energies it is possible to replace the probabilistic relations obtained from the function $\chi(E_1, E_2)$ by an approximate functional dependence (thick solid lines in Fig. 1 *B, C, D*). The above considerations are valid also for an adsorption system consisting of more than two adsorbates.

For the adsorption systems characterized by values of the correlation coefficients close to unity ($|r_{ij}| \approx 1$) it is reasonable to assume that the adsorption energies of all mixture components on different adsorption sites show a qualitatively identical variability. So, the mutually synonymous dependences for the adsorption energies of the *i*-th and *j*-th components may be written

$$E_i = E_i(E_j) \quad \text{and} \quad E_j = E_j(E_i). \quad (5)$$

These dependences are equivalent to the following dependence,

$$\int_{E_{i,min}}^{E_i^*} \chi_i(E_i) dE_i = \int_{E_{j,min}}^{E_j^*} \chi_j(E_j) dE_j = F^*, \quad (6)$$

where the superscript * denotes a definite adsorption site and *F* is the integral distribution function connected with the differential distribution $\chi(E)$ by the simple relationship

$$\frac{dF}{dE} = \chi(E). \quad (7)$$

Introducing Eqs. (5) and (6) into the integral Eq. (1), a single integral is obtained to represent the overall mixed-gas adsorption isotherm; it is:

$$\theta_{i(m)t} = \int_0^1 \theta_{i(m)t}[\mathbf{p}, \mathbf{E}(F)] dF. \quad (8)$$

Then, assuming the local isotherm of the multi-Langmuir type we obtain

$$\theta_{i(m)t} = \int_0^1 \frac{K_{0i} \exp[E_i(F)] p_i}{1 + \sum_{j=1}^n K_{0j} \exp[E_j(F)] p_j} dF, \quad (9)$$

where K_{0i} is the entropy factor.

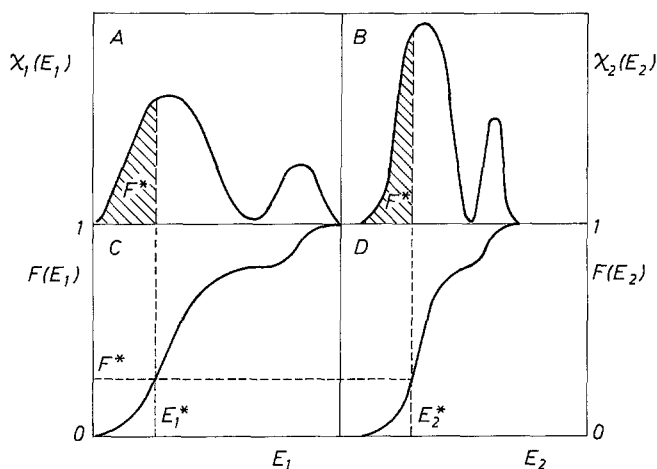


Fig. 2. Comparison between the model differential, $\chi(E)$, and integral, $F(E)$, energy distribution functions

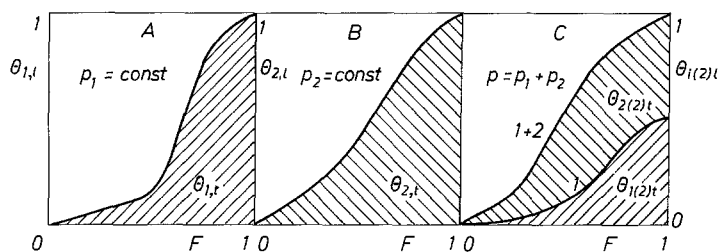


Fig. 3. Dependences between the local surface coverages and the model integral distributions for pure components "1" and "2" and for their mixture

Let us now formulate a new variable

$$z_i(F) = E_i(F) - \bar{E}_i, \quad (10)$$

where \bar{E}_i is the mean adsorption energy.

Introduction of this variable to Eq. (9) gives

$$\theta_{i(n)t} = \int_0^1 \frac{\bar{K}_i p_i \exp[z_i(F)]}{1 + \sum_{j=1}^n \bar{K}_j p_j \exp[z_j(F)]} dF. \quad (11)$$

Here, \bar{K}_i is the Langmuir-type constant connected with the mean adsorption energy \bar{E}_i ; i.e.,

$$\bar{K}_i = K_{0i} \exp(\bar{E}_i); \quad \bar{E}_i = \int_0^1 E_i(F) dF. \quad (12)$$

In order to compare the properties of differential $\chi(E)$ and integral $F(E)$ distribution functions their model graphs are presented in Fig. 2. The distributions presented for two pure components "1" and "2" have two peaks. It is easy to notice that the function $F(E)$ represents a fraction of adsorption sites characterized by the adsorption energies lower than E . In Fig. 3 A, B the dependences between

the local surface coverages $\theta_{i,t}$ and the integral distribution F are shown for the adsorbates "1" and "2" under a constant pressure p_i . The lined areas under the curves denote the total surface coverage $\theta_{i,t}$. However, part C of Fig. 3 presents the same dependence for mixture of both components under a constant pressure $p = p_1 + p_2$.

The new integral equation (11) for the overall adsorption isotherm has a mathematical form, which is very convenient for practical applications. This single integral may be easily solved analytically or numerically; it contains only the quantities characteristic for adsorption of single components, i.e., the mean constants \bar{K}_i and the functions $z_i(F)$. This fact makes a prediction of the mixed-gas adsorption possible for the distribution functions $\chi_i(E_i)$ of different shapes. The previous methods were applicable to the adsorption prediction for the systems characterized by the same type of distributions $\chi_i(E_i)$; this means that Eq. (11) may be used for describing the adsorption systems containing the components, which show different types of adsorption interactions.

Further simplifications of Eq. (11) are possible for gas adsorption over a range of almost full surface coverage, when a competitive adsorption takes place. In such case adsorption may be described in terms of the energy differences for all mixture components. Thus, for adsorption of a binary gas mixture we have

$$\theta_{1(2)t} \approx \int_0^1 \frac{\bar{K}_{12} p_{12} \exp [z_{12}(F)]}{1 + \bar{K}_{12} p_{12} \exp [z_{12}(F)]} dF, \quad (13)$$

where

$$\bar{K}_{12} p_{12} = \bar{K}_1 p_1 / \bar{K}_2 p_2; \quad z_{12}(F) = z_1(F) - z_2(F). \quad (14)$$

When the single-gas adsorption systems forming a mixed-gas adsorption system are characterized by the same type of energy distribution, e.g., the exponential distribution, then the energy dispersion σ_{12} is equal to the difference of dispersions relating to the single-gas adsorption systems, i.e.,

$$\sigma_{12} = \sigma_1 - \sigma_2. \quad (15)$$

This relationship enables a simple estimation of heterogeneity effects in mixed-gas adsorption by using the parameters characterizing single-gas adsorption systems.

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