

The isotherm equations derived for adsorption on heterogeneous surfaces by assuming Jovanović local behaviour

M. JARONIEC and J. PIOTROWSKA

*Department of Theoretical Chemistry, Institute of Chemistry,
M. Curie-Skłodowska University, PL-20-031 Lublin*

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The paper deals with the physical adsorption from gaseous phase on heterogeneous solid surfaces. The monolayer adsorption isotherms for single gases, obtained by solving the fundamental integral equation for Jovanović local isotherm and quasi-gaussian energy distributions, are discussed. These isotherm equations may be extended to multilayer adsorption of single gases and mixed-gas adsorption on heterogeneous solid surfaces.

В работе описана физическая адсорбция из газообразной фазы на гетерогенных твердых поверхностях. Обсуждаются адсорбционные изотермы мономолекулярного слоя для простых газов, полученные решением основного интегрального уравнения Йовановица для локальной изотермы и квази-гауссовой энергии распределения. Эти уравнения изотерм могут применяться к адсорбции многомолекулярного слоя простых газов и к адсорбции смешанных газов на гетерогенных твердых поверхностях.

The isotherm equations describing physical adsorption of single gases on heterogeneous solid surfaces are usually derived by means of the fundamental integral equation [1, 2]

$$\theta_i(p) = \int_{\Delta} \theta(p, \varepsilon) F(\varepsilon) d\varepsilon \quad (1)$$

where $\theta_i(p)$ and $\theta(p, \varepsilon)$ are the overall and local adsorption isotherms, respectively, p is the equilibrium pressure, ε is the adsorption energy, $F(\varepsilon)$ is the energy distribution function normalized to unity, and Δ is the integration region. Eqn (1) was usually solved with respect to $\theta_i(p)$ by using Langmuir local isotherm and different energy distribution functions [1]. The other equation used for describing the local adsorption is so-called Jovanović equation [3]

$$\theta(p, \varepsilon) = 1 - \exp(-Kp) \quad (2)$$

where

$$K = K^0 \exp\left(\frac{\epsilon}{RT}\right) \quad (3)$$

and K^0 is the pre-exponential factor connected with the molecular partition functions of the adsorbate molecules in the surface and bulk phases. Many attempts have been made to derive eqn (2) in terms of the statistical thermodynamics and adsorption kinetics theory [3—11] but its theoretical foundations are still controversial [12].

It is worthwhile to mention that already in 1911 *Schmidt* [13] proposed an equation which leads to Jovanović adsorption isotherm. His idea has been recently undertaken by *Misra* [11]. Also, in 1946 *Temkin* and *Levich* [14] proposed the Jovanović-type isotherm equation for describing the adsorption kinetics (see also the references [15—17]). Their theoretical considerations have been applied by *Budrugaec* [10] for deriving the isotherm eqn (2). Moreover, eqn (2) has been widely examined by using gas adsorption data [18—20]. Eqn (2) was also applied to derive the relationships describing gas chromatographic data [21, 22]. Its extension to mixed-gas adsorption was proposed by *Jaroniec* [23, 24], *Popa* and *Segal* [25]. An experimental verification of Jovanović-type equations describing mixed-gas adsorption has been recently presented by *Longauer et al.* [26].

Many authors [27—34] used eqn (2) for describing the local adsorption isotherm appearing in the integral eqn (1). In Ref. [27, 28] the condensation approximation method was used to solve the integral eqn (1) with Jovanović eqn (2). The numerical methods of solving the integral eqn (1) with the local isotherm (2) were discussed by *Rudziński* and *Jaroniec* [29]. However, analytical solutions of eqn (1) for constant and exponential energy distributions were presented by *Misra* [30]. The isotherm equations derived by *Misra* [30] were also extended to multilayer gas adsorption [34] and mixed-gas adsorption on heterogeneous surfaces [35—37]. Unfortunately, *Misra* [30] solved eqn (1) with the local isotherm (2) only for two simple energy distributions, which are not typical distributions obtained from experimental adsorption data. In this paper, we shall discuss analytical solutions of the integral eqn (1) with the local isotherm (2) for quasi-gaussian energy distributions, which are typical for many gas—solid adsorption systems [1].

Monolayer adsorption of single gases

The integral representation of the overall adsorption isotherm for Jovanović local behaviour may be expressed as follows

$$\theta_i(p) = 1 - \int_{\epsilon^*}^{\infty} \exp(-Kp) F(\epsilon) d\epsilon \quad (4)$$

where ε' is the minimum adsorption energy. Eqn (4) has been obtained from eqns (1) and (2).

Let us introduce the new variable

$$k = K - K' \tag{5}$$

where

$$K' = K^0 \exp\left(\frac{\varepsilon'}{RT}\right) \tag{6}$$

and

$$d\varepsilon = \frac{RT}{K' + k} dk \tag{7}$$

The integration region (ε', ∞) is transformed on the interval $(0, \infty)$ with respect to k .

Thus, the integral eqn (4) may be rewritten as follows

$$\theta_i(p) = 1 - \exp(-K'p) \int_0^\infty \exp(-kp) G(k) dk \tag{8}$$

where

$$G(k) = \frac{RT}{K' + k} F \left[RT \ln \left(\frac{k + K'}{K^0} \right) \right] \tag{9}$$

Many of the physically realistic functions $G(k)$ may be obtained from the following general equation

$$G(k) = Nk^m \exp(-qk^n) \tag{10}$$

where N is the normalization factor and q, m, n are parameters greater than zero.

Eqns (8) and (10) give

$$\theta_i(p) = 1 - N \exp(-K'p) \int_0^\infty k^m \exp(-kp - qk^n) dk \tag{11}$$

Eqn (11) may be analytically solved for some sets of values of m and n . In the case of $n=1$ and m greater than zero eqn (11) gives

$$\theta_i(p) = 1 - \left(\frac{q}{q+p} \right)^{m+1} \exp(-K'p) \tag{12}$$

In other words, eqn (12) is the solution of eqn (8) for gamma-type distribution

$$G(k) = \frac{q^{m+1}}{\Gamma(m+1)} k^m \exp(-qk) \tag{13}$$

For $m = 0$ this distribution becomes a simple exponential decreasing function of k

$$G(k) = q \exp(-qk) \quad \text{for } k > 0 \quad (14)$$

However, the exponential distribution (14) transformed by means of eqns (3), (6), and (9) gives the energy distribution $F(\varepsilon)$ of quasi-gaussian shape (Fig. 1). Analytical form of the energy distribution obtained from eqn (14) is

$$F(\varepsilon) = \frac{qK^0}{RT} \exp\left(\frac{\varepsilon}{RT}\right) \exp\left\{-qK^0 \left[\exp\left(\frac{\varepsilon}{RT}\right) - \exp\left(\frac{\varepsilon'}{RT}\right)\right]\right\} \quad (15)$$

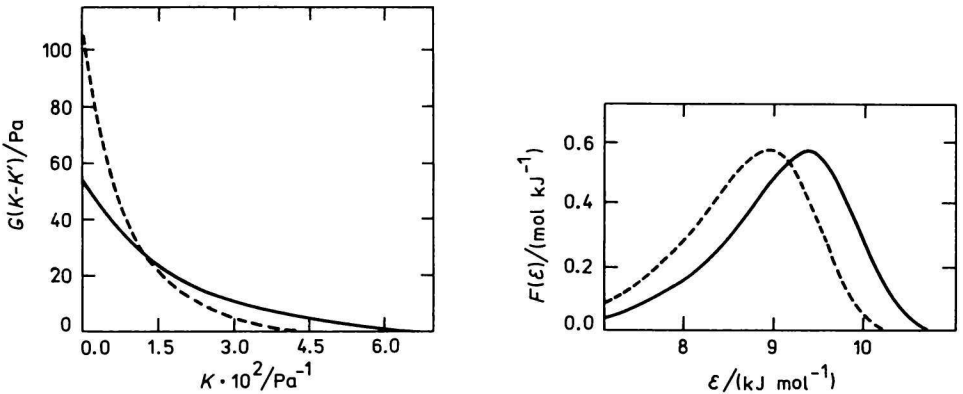


Fig. 1. Distributions $G(K - K')$ and $F(\varepsilon)$ calculated according to eqns (14) and (15), respectively, for $K^0 = 0.95 \times 10^{-8} \text{ Pa}^{-1}$, $K' = 1.523 \times 10^{-4}$, and $q = 53.3 \text{ Pa}$ (the solid line) and 106.6 Pa (the dashed line).

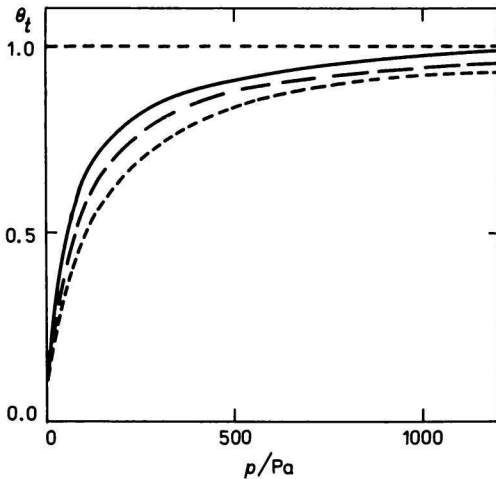


Fig. 2. Adsorption isotherms calculated according to eqn (16) for $K' = 1.523 \times 10^{-4} \text{ Pa}^{-1}$ and $q = 53.3 \text{ Pa}$ (the solid line), 75.0 Pa (the weakly dashed line), and 106.6 Pa (the strongly dashed line).

The adsorption isotherm corresponding to the energy distribution (15), which is generated by eqn (14), may be obtained from eqn (12) and $m = 0$; it is

$$\theta_i(p) = 1 - \left(\frac{q}{q + p} \right) \exp(-K'p) \quad (16)$$

The model adsorption isotherms calculated according to eqn (16) are shown in Fig. 2; the adsorption increases with the greater adsorbent heterogeneity.

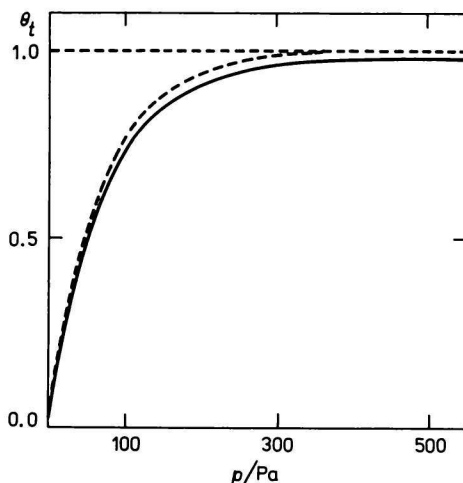


Fig. 3. Adsorption isotherms calculated according to eqn (21) for parameters $K' = 1.5 \times 10^{-2} \text{ Pa}^{-1}$ and $q = 2 \times 10^6 \text{ Pa}^2$ (the dashed line) and $2 \times 10^4 \text{ Pa}^2$ (the solid line).

The second important solution of eqn (11) is obtained for $m = 1$ and $n = 2$. For these values of m and n eqn (10) produces the so-called Rayleigh-type distribution function

$$G(k) = 2qk \exp(-qk^2) \quad (17)$$

This distribution gives the following equation for the overall adsorption isotherm

$$\theta_i(p) = 1 - \exp(-K'p) \left[1 - \frac{p}{2} \sqrt{\frac{\pi}{q}} - \exp\left(\frac{p^2}{4q}\right) \operatorname{erf}\left(\frac{p}{2\sqrt{q}}\right) \right] \quad (18)$$

where the symbol "erf" denotes the error function.

Eqn (10) for $m = 0$ and $n = 2$ produces Gaussian distribution; in this case K' denotes the value for which the normal distribution reaches the maximum. The normal distribution

$$G(k) = \sqrt{\frac{q}{\pi}} \exp(-qk^2) \quad (19)$$

gives the adsorption isotherm of the following form

$$\theta_i(p) = 1 - \exp(-K'p) \exp\left(\frac{p^2}{4q}\right) [1 - \operatorname{erf}(y)]/2 \quad (20)$$

where $\operatorname{erf}(y)$ is the error function and $y = (p - 2qK')/(2\sqrt{q})$. The term containing the error function may be neglected and then we have

$$\theta_i(p) = 1 - \exp\left(-K'p + \frac{p^2}{4q}\right) \quad (21)$$

The model adsorption isotherms calculated according to eqn (21) are presented in Fig. 3. The energy distribution function corresponding to the isotherm eqn (21), obtained by transformation of eqn (19), is

$$F(\varepsilon) = \sqrt{\frac{q}{\Pi}} \frac{K^0}{RT} \exp\left(\frac{\varepsilon}{RT}\right) \exp\left\{qK^{02} \left[\exp\left(\frac{\varepsilon}{RT}\right) - \exp\left(\frac{\varepsilon'}{RT}\right)\right]^2\right\} \quad (22)$$

The distribution functions calculated according to eqns (19) and (22) are shown in Fig. 4. As it is illustrated in the figure, the symmetrical function of k is transformed to the asymmetrical function of ε with a widening in the direction of low adsorption energies.

Monolayer mixed-gas adsorption

In Ref. [24] eqn (2) has been extended to mixed-gas adsorption on homogeneous solid surfaces. The extended form of eqn (2) may be written as follows

$$\theta_i(p_1, p_2, \dots, p_r) = 1 - \exp\left(-\sum_{i=1}^r K_i p_i\right) \quad (23)$$

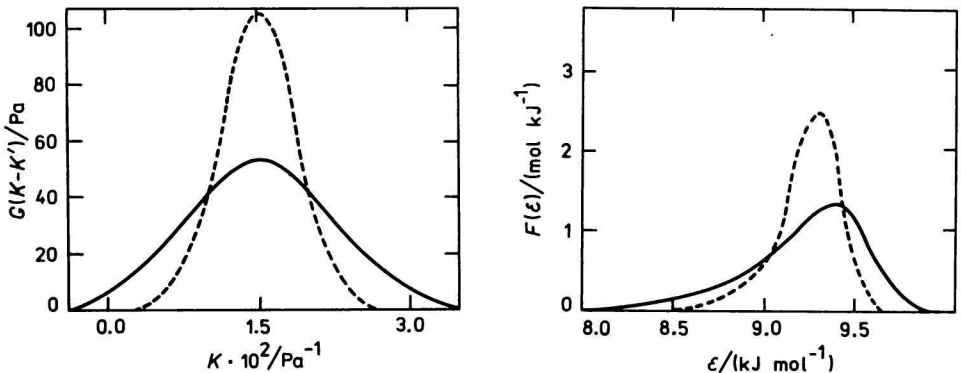


Fig. 4. Distributions $G(K-K')$ and $F(\varepsilon)$ calculated according to eqns (19) and (22), respectively, for $K^0 = 0.95 \times 10^{-8} \text{ Pa}^{-1}$, $K' = 1.5 \times 10^{-2} \text{ Pa}^{-1}$, and $q = 3.555 \times 10^4 \text{ Pa}^2$ (the dashed line) and $8.888 \times 10^3 \text{ Pa}^2$ (the solid line).

where θ_r denotes the total adsorption of r components, p_i is the partial pressure of the i -th component, and K_i is the constant (3) for the i -th gas. The generalized integral equation, proposed by Jaroniec [35] for describing the mixed-gas adsorption on heterogeneous surfaces, in the case of Jovanović local isotherm (23) gives the following relationship

$$\theta_{r,t}(p_1, p_2, \dots, p_r) = 1 - \prod_{i=1}^r \theta_{i,t}(p_i) \quad (24)$$

where $\theta_{r,t}$ is the total adsorption isotherm for r components on a heterogeneous surface, and $\theta_{i,t}(p_i)$ is the single-gas adsorption isotherm of the i -th component. Thus, the monolayer mixed-gas adsorption isotherms for heterogeneous surfaces may be obtained by using single-gas isotherms discussed in the previous section, e.g. eqns (12), (16), (18), and (20). As an example we present the isotherm for binary gas mixtures obtained by means of eqns (16) and (24)

$$\begin{aligned} \theta_{2,t}(p_1, p_2) = & \frac{q_1}{q_1 + p_1} \exp(-K'_1 p_1) + \frac{q_2}{q_2 + p_2} \exp(-K'_2 p_2) - \\ & - \frac{q_1}{q_1 + p_1} \cdot \frac{q_2}{q_2 + p_2} \exp(-K'_1 p_1 - K'_2 p_2) \end{aligned} \quad (25)$$

where q_i and K'_i are the constants q and K , respectively, referring to the i -th component.

The second possibility of extending eqn (23) to adsorption on heterogeneous surfaces was discussed in Ref. [38]. This method may be applied to the systems fulfilling the following condition

$$K_i/K_1 = A_i \quad \text{for } i=2, 3, \dots, r \quad (26)$$

and A_i is the constant characteristic of the entire solid surface. According to this method the single-gas isotherms, discussed in the previous section, may be extended to the mixed-gas adsorption by replacing in them the constant K' by K'_i and pressure p by the following expression

$$x_r = p_1 + \sum_{i=2}^r (K_i/K_1) p_i \quad (27)$$

As an example we present the adsorption isotherm for binary gas mixtures obtained by extending eqn (16) according to the method in question

$$\theta_{2,t}(p_1, p_2) = 1 - \frac{q_1}{q_1 + \left(p_1 + \frac{K_2}{K_1} p_2\right)} \cdot \exp \left[K'_1 \left(p_1 + \frac{K_2}{K_1} p_2 \right) \right] \quad (28)$$

The isotherm eqn (28) presented as a function of x_r , has quite analogous form as the

single-gas adsorption isotherm (16). The second method leads to simpler isotherm equations for mixed-gas adsorption and is usually used in practice [1].

Extension to multilayer adsorption

The monolayer single-gas and mixed-gas adsorption isotherms may be also extended to multilayer adsorption. The method of their generalization may be analogous to that presented in the review [1]. According to this method the monolayer adsorption isotherms, derived for heterogeneous surfaces, should be multiplied by the function describing the multilayer formation, which is assumed to be independent of the adsorbent heterogeneity. This function for single-gas adsorption has simple exponential form [18]

$$h(p) = \exp(bp) \quad (29)$$

where b is the constant characterizing the multilayer adsorption. For mixed-gas adsorption the function describing multilayer formation may be written in the form [24]

$$h_r(p_1, p_2, \dots, p_r) = \exp\left(\sum_{i=1}^r b_i p_i\right) \quad (30)$$

where b_i is the constant b referring to the i -th component.

The adsorption isotherms discussed in this paper may be also generalized to liquid adsorption by utilizing the analogy between gas and liquid adsorption [1]. It follows from the review [1] that isotherm equations describing gas and liquid adsorption are analogous from the mathematical point of view. According to the procedure discussed in the review [1] the isotherm equations for adsorption from dilute solutions may be obtained from gas adsorption isotherms by replacing in them the pressure p_i by solute concentrations c_i .

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