Monatshefte für Chemie 117, 7—19 (1986)

**Monatshefte für Chemie**
**Chemical Monthly**

# Isotherm Equations for Adsorption on Heterogeneous Microporous Solids

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*(Received 19 March 1984. Accepted 21 January 1985)*

The overall isotherm equations have been derived for adsorption from gaseous and liquid phases on heterogeneous microporous solids by solving *Stoeckli*'s integral equation. In this integral the *Dublin-Radushkevich* equation is used to describe the local adsorption on micropores having identical shape and dimensions. The above integral has been solved for different types of distribution functions characterizing heterogeneity of microporous structure of the solids.

*(Keywords: Adsorption on heterogeneous microporous solids; Gas adsorption on solids; Liquid adsorption on solids; Structural heterogeneity of solids)*

*Adsorptionsisothermen für heterogene mikroporöse Feststoffe*

Es wurden Isothermengleichungen für die Adsorption aus Gas- oder Flüssigphasen an heterogenen mikroporösen Feststoffen mittels der Lösung von *Stoeckli*'s Integralgleichung abgeleitet. In diesem Integral wurde die *Dubinin-Radushkevich*-Gleichung für die Beschreibung der lokalen Adsorption an Mikroporen mit identem Umriß und identer Größe benutzt. Das oben erwähnte Integral wurde für verschiedene Typen von Verteilungsfunktionen, die die Heterogenität der mikroporösen Strukturen von Festkörpern charakterisieren, gelöst.

## Introduction

Many years ago *Dubinin* and *Radushkevich*[1] proposed an equation for describing the physical adsorption of single gases on microporous solids, which is one of the most popular isotherm equations in the adsorption theory[2—8]. This isotherm, called the *Dubinin-Radushkevich* (*DR*) equation, was widely used to describe the experimental data of adsorption of single gases and vapours on microporous solids[2,3]. In 1965 *Izotova* and *Dubinin*[9] postulated that the *DR* equation applies only to solids with an uniform structure of micropores and considered the case of an adsorbent showing bimodal microporous structure. Then the overall adsorption isotherm is a simple sum of two contributions, where each of them is a product of the volume ratio of a given class of micropores and the *DR* equation describing the adsorption process in these micropores[9]. In the case of solids showing a greater number of different classes of micropores the overall adsorption isotherm contains more of such contributions and when their number increases to infinity the summation may be replaced by integration. The integral form of the overall isotherm for single-gas adsorption on heterogeneous microporous solids has been firstly proposed by *Stoeckli*[10]; it is

$$\theta_t(p) = \int_{\Delta} \theta(p, B) F(B) \, \mathrm{d} B \tag{1}$$

where $\theta_t(p)$ is the overall adsorption isotherm for heterogeneous microporous solids; $\theta(p, B)$ is the isotherm describing local adsorption in micropores of a given class characterized by the structural parameter $B$; $p$ is the equilibrium pressure; $F(B)$ is the distribution function characterizing heterogeneity of the micropore volume with respect to the structural parameter $B$; $\Delta$ is the integration region. The function $F(B)$ fulfils the normalization condition:

$$\int_{\Delta} F(B) \, \mathrm{d} B = 1 \tag{2}$$

Moreover, this function has a clear physical meaning because the structural parameter $B$ is proportional to $r^2$, where $r$ is the characteristic dimension of a given class of micropores, e.g., in the case of disk-shaped micropores the so-called inertia radius of the micropores $R$ depends on the height $2r$ and on the diameter $2r'$ of the base[11]. Postulating to a first approximation that $R$ is proportional to $r$ we obtain proportionality between $B$ and $r^2$, i.e.[11]:

$$B(r) = C r^2 \tag{3}$$

where $C$ is the proportionality constant.

It is easy to see that the distribution function of micropore volume with respect to the characteristic dimension $r$, $G(r)$, is expressed as follows[11]:

$$G(r) = F\big(B(r)\big) \frac{\mathrm{d} B(r)}{\mathrm{d} r} \tag{4}$$

Eq. (4) combined with Eq. (3) gives:

$$G(r) = 2 C r F\big(B(r)\big) \tag{5}$$

*Dubinin* and *Stoeckli*[11] recalculated the *Gauss*ian distribution $F(B)$ on the distribution $G(r)$. The symmetral *Gauss*ian distribution $F(B)$ is transformed according to Eq. (5) to the asymmetrical function $G(r)$ with a widening in the direction of smaller values of $r$.

Let us return to the local adsorption isotherm $\theta(p, B)$ appearing in Eq. (1). According to the postulate of *Izotova* and *Dubinin*[9], and *Stoeckli*[10] the *DR* equation may be used for describing the local adsorption in a given class of micropores; it is[1]:

$$\theta(p, B) = \exp(-By) \tag{6}$$

where

$$y = [RT \ln(p_0/p)]^2 \text{ for } p \leqslant p_0 \tag{7}$$

and $p/p_0$ is the relative pressure. The structural parameter $B = B^*/\alpha$, where $B^*$ characterizes only the solid, whereas the parameter $\alpha$ is the so-called affinity coefficient depending only on the adsorptive.

Eq. (6) has been extended to mixed-gas adsorption[12, 13]. In contrast to the extensive literature concerning studies of gas adsorption by means of Eq. (6), liquid adsorption has been comparatively less studied in the terms of this formulation. *Koganovski* et al.[14], *Jaroniec* and *Derylo*[15–17] used the *DR*-type equation to describe the adsorption of organic substances from dilute aqueous solutions on activated carbons; moreover, *Jaroniec* et al.[4, 5, 18–20] proposed an analogous expression to Eq. (6) for describing adsorption of liquid mixtures of nonelectrolytes in the whole concentration range.

In this paper we shall discuss the overall single-gas adsorption isotherms for heterogeneous microporous solids obtained by means of the integral Eq. (1) for different distribution functions $F(B)$. These isotherm equations will be extended to adsorption from dilute solutions and adsorption from liquid mixtures of nonelectrolytes in the whole concentration region. Moreover, this paper will bring some further generalizations of *Stoeckli*'s approach[10] and their critical discussion.

## Results and Discussion

### *Single-Gas Adsorption on Heterogeneous Microporous Solids*

The fundamental equation describing single-gas adsorption on heterogeneous microporous solids is the integral Eq. (1) with the local isotherm Eq. (6)[10]:

$$\theta_t(p) = \int_{\Delta} \exp(-By) F(B) \, \mathrm{d} B \tag{8}$$

The integral Eq. (8) may be solved for many analytical functions $F(B)$. Many of the physically realistic functions may be obtained from the following general equation:

$$F(B) = N(B - B_0)^m \exp[-q(B - B_0)^n] \tag{9}$$

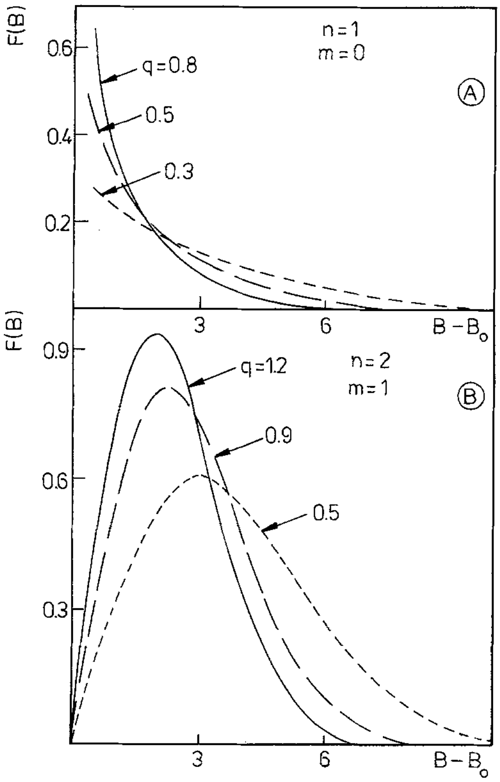

Fig. 1. The distribution curves calculated according to Eq. (9) for $n = 1, m = 0$ ($A$), $n = 2$, $m = 1$ ($B$) and different values of $q$

Table 1. *Distribution functions being special cases of Eq. (9)*

| Name of distribution | $m$ | $n$ | $N$ |
|---|---|---|---|
| exponential d. | 0 | 1 | $q$ |
| gamma-function 1 | $>0$ | 1 | $q^{m+1}/\Gamma(m+1)$ |
| *Maxwell-Boltzmann* d. | 0.5 | 1 | $2\pi^{-1/2} \cdot q^{3/2}$ |
| *Gauss*ian d. | 0 | 2 | $(q/\pi)^{1/2}$ |
| *Rayleigh* d. 1 | 1 | 2 | $2q$ |
| *Rayleigh* d. 2 | $n$—1 | $\geqslant 1$ | $nq$ |
| gamma-function 2 | $>0$ | 2 | $2q^{(m+1)/2}/\Gamma\left(\frac{m+1}{2}\right)$ |

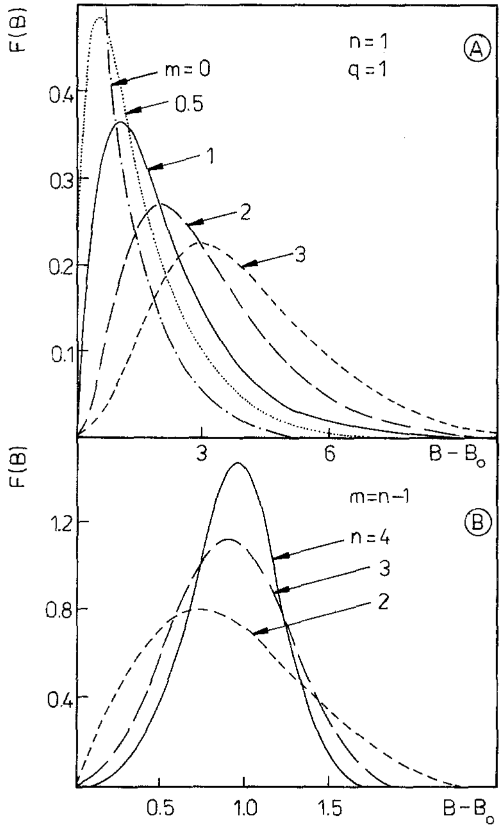

Fig. 2. The distribution curves calculated according to Eq. (9). *A*: $q = 1$, $n = 1$ and different values of $m$. *B*: $q = 0.9$, $m = n$-1 and different values of $n$

where $N$ is the normalization factor assuring the fulfilment of the condition given by Eq. (2); $B_0$ is the characteristic value of $B$ for a given distribution function; and $q$, $m$ and $n$ are parameters greater than zero. For different values of $m$ and $n$ Eq. (9) gives simpler expressions, which may be used to characterize the heterogeneity of microporous structure of the solid adsorbents. These expressions are summarized in Table 1.

Figs. 1 and 2 show the influence of parameters $m$, $n$ and $q$ on the shape of the distribution $F(B)$. The exponential distribution [Eq. (9) with $m = 0$ and $n = 1$] and the *Rayleigh* distribution [Eq. (9) with $m = 1$ and $n = 2$] are presented in Fig. 1; the first of them is a decreasing function, whereas the second function shows a quasi-*Gauss*ian course with a widening to the right-hand side. It follows from this figure that the parameter $q$ determines only the width of the function $F(B)$ and it may be called the heterogeneity parameter; decrease in its value causes an increase in the structural heterogeneity of the solid [the width of $F(B)$ increase]. The influence of parameters $m$ and $n$ on the course of the function $F(B)$ is more complicated. These parameters determine simultaneously shape and width of $F(B)$. Fig. 2 *A* shows the curves $F(B)$ calculated according to Eq. (9) for $n = 1$, $q = 1$ and different values of $m$. It follows from this figure that for $m = 0$ the function $F(B)$ is exponential, for $m = 0.5$ and 1 it is similar to curves presented in Fig. 1 *B*, i.e., it shows a strong widening to the right-hand side; however, for $m = 2, 3$ it becomes a more symmetrical distribution. Moreover, an increase in the value of $m$ causes an increase in the structural heterogeneity of the solid because the width of $F(B)$ becomes greater. Fig. 2 *B* shows the curves $F(B)$ for $m = n—1$, $q = 0.9$ and different values of $n$. In this case an increase in the value of $n$ causes a decrease in the structural heterogeneity; thus, this effect is opposite in comparison to that due to the parameter $m$. However, the dependence between values of $n$ and shape of $F(B)$ is analogous as in the case of the parameter $m$, i.e., for greater values of $n$ the function $F(B)$ becomes more symmetrical and already for $n = 4$ it is quite similar to a *Gauss*ian distribution which is also obtained from Eq. (9) for $m = 0$ and $n = 2$.

Analogous equations to those summarized in Table 1 were used to describe the energetic heterogeneity of the solid surface. The exponentially decreasing distribution was applied by many authors (see the references in the reviews[3,5,7]), e.g., *Rudnitsky* and *Alexeyev*[21], *Appel*[22] and *Misra*[23]; it is an asymmetrical function. In contrast to it, a *Gauss*ian distribution is fully symmetrical. This distribution was widely used by *Ross* and *Olivier*[24] to describe energetic heterogeneity. The other distribution used in gas adsorption on energetically heterogeneous surfaces, such as: *Maxwell-Boltzmann, Rayleigh* and gamma-type functions were applied by *Kindl* et al.[25,26], *Cerofolini*[27], *Misra*[28], *Smutek*[29,30] and *Sircar*[31]. The above discussion suggests that the distribution functions summarized in Table 1 should be useful for characterizing the heterogeneity of microporous structure of the solids because their analogues are applied successfully for describing the energetic heterogeneity of the solid surfaces. Experimental studies of *Stoeckli* et al.[11,32—35] dealing with the application of the *Gauss*ian distribution $F(B)$ for characterizing the heterogeneity of microporous structure of the solids confirm great utility of Eq. (8) for describing gas/solid adsorption systems.

Integration of the integral Eq. (8) for $\Delta = (0, \infty)$ and *Gauss*ian distribution $F(B)$, i.e., Eq. (9) with $m = 0$ and $n = 2$, gives[10]:

$$\theta_t(p) = \exp(—B_0 y)\exp(y^2/4q)[1—erf(w)]/2 \qquad (10)$$

where the variable $y$ is the function of $p$ defined by Eq. (7); $w = (y—2qB_0)/2\sqrt{q}$ and $erf(w)$ is the error function.

Substitution of Eq. (9) into Eq. (8) with $\Delta = (B_0, \infty)$, where $B_0$ is the minimal value of $B$, and introduction of a new variable $\beta = B - B_0$ gives:

$$\theta_t(p) = N \exp(-B_0 y) \int_0^\infty \beta^m \exp(-y\beta - q\beta^n)\,\mathrm{d}\beta \tag{11}$$

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

$$\theta_t(p) = \exp(-B_0 y)\left(\frac{q}{q+y}\right)^{m+1} \tag{12}$$

In other words, Eq. (12) is the solution of the integral Eq. (8) for gamma-function "1" summarized in Table 1.

For the exponential distribution ($m = 0$) this solution assumes the form:

$$\theta_t(p) = \exp(-B_0 y)\frac{q}{q+y} \tag{13}$$

For values of $p$ tending to $p_0$ the variable $y$ tends to zero and then Eq. (13) becomes:

$$\theta_t(p) = \frac{q}{q+y} \tag{14}$$

Eq. (14) may be easily linearized with respect to the variable $y$ defined by Eq. (7). However, expanding $\exp(B_0 y)$ into *Taylor* series and taking into account in Eq. (13) only two first terms of this series, we have:

$$\theta_t(p) = \frac{q}{(1 + B_0 y)(q + y)} \tag{15}$$

or

$$\frac{1}{\theta_t(p)} = 1 + (B_0 + 1/q)y \tag{16}$$

Eqs. (14) and (16) may be useful to determine the approximate values of $q$, $B_0$, and surface phase capacity from adsorption data.

Eq. (11) may be also solved for *Rayleigh* distribution "1", i.e., Eq. (9) with $m = 1$ and $n = 2$. Then we obtain[36, 37]:

$$\theta_t(p) = \exp(-B_0 y); \left[1 - \frac{y}{2}\sqrt{\frac{\pi}{q}} \exp\left(\frac{y^2}{4q}\right) erf\left(\frac{y}{2\sqrt{q}}\right)\right] \tag{17}$$

The overall adsorption isotherms, Eqs. (10), (12) and (17), contain the function $\exp(-B_0 y)$, which is *DR* Eq. (6) referring to the value $B = B_0$.

Now, we shall propose an approximate method for solving the integral

Eq. (8) analogous to that used in gas adsorption on energetically heterogeneous surfaces[39]. According to this method the local isotherm $\exp(-By)$ is replaced by a step function, which suddenly changes from unity to zero as the variable $y$ exeeds a "condensation value" $y_c$. Then the integral Eq. (8) may be easily solved with respect to the distribution function. This function may be calculated according to the following relationship:

$$F_c(B_c) = \frac{d\,\theta_t(p(B_c))}{d\,B_c} \tag{18}$$

where $p(B_c)$ is evaluated by means of the relationship analogous to that proposed by *Cerofolini*[39]; it is:

$$\exp(-By_c) = 0.5 \tag{19}$$

where $y_c$ is defined analogously as in Eq. (7). The subscript "$c$" at the symbols appearing in Eq. (18) denotes that this equation has been derived from Eq. (8), in which the function $\exp(-By)$ has been replaced by the step function. The relationship $p(B_c)$ obtained from Eq. (19) is:

$$y = [RT\ln(p_0/p)]^2 = 0.6931/B_c \tag{20}$$

Applying Eqs. (18) and (20) for a known isotherm equation, representing single-gas adsorption on heterogeneous microporous solids, we can calculate the approximate distribution function $F_c(B_c)$. The error occurring in this method of evaluation of the function $F_c(B_c)$ may be estimated as follows. According to *Stoeckli*'s postulate[10], the isotherm Eq. (6) describes single-gas adsorption on a homogeneous microporous solid; it means that the solid is characterized by the *Dirac* distribution of $B$. However, treating Eq. (6) as the overall adsorption isotherm we can calculate the distribution function $F_c(B_c)$ by means of Eqs. (18) and (20); it is:

$$F_c(B_c) = (0.6931\,B/B_c^2)\exp(-0.6931\,B/B_c) \text{ for } B_c > 0 \tag{21}$$

The function $F_c(B_c)$ given by Eq. (21) shows a maximum at $B_c = 0.3465\,B$ and differs from the *Dirac* function. The difference between the *Dirac* function and Eq. (21) shows what error is introduced by the approximate method of evaluation of $F(B)$ based on Eqs. (18) and (20).

Although Eq. (6) describes single-gas adsorption on homogeneous microporous solids, i.e., solids characterized by a *Dirac* function with respect to $B$, these solids are energetically heterogeneous. *Cerofolini*[27] found the energy distribution function corresponding to Eq. (6); it is:

$$\chi^{DR}(\varepsilon) = 2\,B(\varepsilon-\varepsilon_0)\exp[-B(\varepsilon-\varepsilon_0)^2] \text{ for } \varepsilon \geqslant \varepsilon_0 \tag{22}$$

where $B$ determines the width of the function given by Eq. (22) and $\varepsilon_0$ determines its position on the energy axis. This function has quasi-

*Gauss*ian shape and is widened in the direction of the higher adsorption energies. It has been obtained by using *Cerofolini*'s relationship[27] to the isotherm Eq. (6); they are:

$$\chi^{DR}(\varepsilon) = -\frac{\mathrm{d}}{\mathrm{d}\,\varepsilon}\exp\left[-B(\varepsilon-\varepsilon_0)^2\right] \tag{23}$$

where

$$\varepsilon-\varepsilon_0 = RT\ln(p_0/p) \tag{24}$$

Eq. (23) has been obtained in terms of a general relationship derived for gas adsorption on energetically heterogeneous surfaces[39] defining the energy distribution function as the negative derivative of the overall isotherm with respect to $\varepsilon$, in which the pressure $p$ has been expressed as a function of $\varepsilon$ by means of Eq. (24). Using this general relationship to Eq. (8) we have:

$$\chi(\varepsilon) = -\frac{\mathrm{d}\,\theta_t}{\mathrm{d}\,\varepsilon} = \int_{\Delta} 2B(\varepsilon-\varepsilon_0)\exp\left[-B(\varepsilon-\varepsilon_0)^2\right]F(B)\,\mathrm{d}\,B \tag{25}$$

Some authors[36] calculated the energy distribution functions corresponding to the overall adsorption isotherms, e.g., Eqs. (10), (13), and (17), by a simple differentiation ($-\mathrm{d}\,\theta_t/\mathrm{d}\,\varepsilon$). Eq. (25) indicates that their physical interpretation is complex because they contain the energy distributions given by Eq. (22) related to each value of $B$. As example we will consider a solid showing some classes of micropores characterized by the parameters $B_1, B_2, \ldots, B_s$. Then the distribution function is expressed as follows:

$$F(B) = \sum_{i=1}^{s} h_i\,\delta(B-B_i) \tag{26}$$

where

$$\delta(B-B_i) = \begin{cases} 0 \text{ for } B \neq B_i \\ 1 \text{ for } B = B_i \end{cases} \tag{27}$$

and

$$\sum_{i=1}^{s} h_i = 1 \tag{28}$$

Eqs. (25) and (26) give:

$$\chi(\varepsilon) = -\frac{\mathrm{d}\,\theta_t}{\mathrm{d}\,\varepsilon} = \sum_{i=1}^{s} 2h_iB_i(\varepsilon-\varepsilon_0)\exp\left[-B_i(\varepsilon-\varepsilon_0)^2\right] \tag{29}$$

Eq. (29) shows that the energy distribution function $\chi(\varepsilon)$ evaluated from adsorption data for heterogeneous microporous solids gives a global information about energetic heterogeneity generated by microporous structure of the solid. In the case of real adsorption systems the interpretation of $\chi(\varepsilon)$ is yet more difficult because it also contains the information about energetic heterogeneity generated by surface imperfections and surface functional groups.

### *Adsorption of Liquid Mixtures on Heterogeneous Microporous Solids*

In this section we shall briefly present the possibility of extending Eqs. (10), (12), (13), and (17) to adsorption from dilute and concentrated solutions on heterogeneous microporous solids. Analogous isotherm equations to Eq. (6) may be used for describing liquid adsorption from dilute and concentrated solutions. These equations differ from Eq. (6) in definition of the variable $y$. According to the review[5] the variable $y$ is defined as follows:

$$y = [RT \ln (c_0/c)]^2 \text{ for } c \leqslant c_0 \tag{30}$$

for adsorption from dilute solutions, and

$$y = [RT \ln (x_0/x_{12}^1)]^2 \text{ for } x_{12}^1 \leqslant x_0 \tag{31}$$

for adsorption of binary liquid mixtures of nonelectrolytes.

In the above $c$ is the solute concentration; $x_{12}^1 = x_1^1/x_2^1$ is the ratio of mole fractions of components "1" and "2" in the bulk solution; $c_0$ and $x_0$ are parameters.

In the case of liquid adsorption in the whole concentration region the mole fraction of the first component in the surface phase, $x_1^s$, plays an analogous role as the relative surface coverage in the gas adsorption; thus, we can write:

$$x_1^s = \exp(-By) \text{ for } x_{12}^1 \leqslant x_0 \tag{32}$$

and for $x_{12}^1 > x_0$ the mole fraction $x_1^s$ is approximated by unity. The symbol $y$ appearing in Eq. (32) is defined by Eq. (31). Moreover, Eq. (32) is valid for adsorption of liquid mixtures containing components of identical molecular sizes[6].

For the purpose of illustration we shall write an analogue of Eq. (12) for solute adsorption from dilute solutions on heterogeneous microporous solids:

$$\theta_t(c) = \exp[-B_0 y(c)] \left[\frac{q}{q + y(c)}\right]^{m+1} \tag{33}$$

where $y(c)$ is given by Eq. (30), and for liquid adsorption from concentrated solutions:

$$x_1^s(x_{12}^1) = \exp[-B_0 y(x_{12}^1)] \left[\frac{q}{q + y(x_{12}^1)}\right]^{m+1} \tag{34}$$

where $y(x_{12}^1)$ is expressed by Eq. (31).

Eqs. (10) and (17) may be extended analogously. The special cases of Eqs. (33) and (34) were examined by *Jaroniec* et al.[40, 41]. Moreover, Eqs. (10), (12), and (17) may be easily generalized to adsorption from multicomponent mixtures on heterogeneous microporous solids. In the reviews[5, 6] the *DR*-type equations are discussed for adsorption from multicomponent mixtures and these equations may be presented in the mathematical form as Eq. (6); of course, the variable $y$ has another definition taking into account concentrations of all components in the bulk phase. Definitions of $y$ for adsorption from multicomponent mixtures are given in the reviews[5, 6].

### *A Modification of Stoeckli's Approach*

The fundamental equation in *Stoeckli*'s approach[10] is the integral Eq. (8), which has been proposed by assuming the postulate that *DR* Eq. (6) describes adsorption on homogeneous microporous solids. *Suzuki* and *Sakoda*[38] and *Rozwadowski* and *Wojsz*[36, 37] postulate *Dubinin-Astakhov* (*DA*) equation[42] to describe the local adsorption; it is:

$$\theta(p, B) = \exp\left[\ B\left(RT\ln\frac{p_0}{p}\right)^{v}\right] \tag{35}$$

where the exponent $v$ modifies the earlier formulation of theory of micropore filling as expressed by Eq. (6).

Substituting Eq. (35) into Eq. (1) we obtain the integral Eq. (8), in which $y$ is defined as follows:

$$y = \left(RT\ln\frac{p_0}{p}\right)^{v} \tag{36}$$

According to this modification the isotherm Eqs. (10), (12), and (17) contain the variable $y$ defined by Eq. (36).

### *Concluding Remarks*

Series papers[11, 32—37, 40, 41] developing the *Stoeckli*'s conception[10] of microporous structure heterogeneity of the solids have been published. Taking into account up-to-date theoretical achievements in this field we presented an unified treatment of adsorption from gaseous and liquid phases on heterogeneous microporous solids, which is analogous to that proposed for adsorption on energetically heterogeneous surfaces[5]. According to this treatment the single-gas adsorption isotherm Eqs. (10), (12), and (17) may be easily extended to adsorption from dilute and concentrated solutions by using Eqs. (30) and (31) for defining the variable $y$.

Although simplest cases of Eq. (12) were examined by using liquid adsorption data[40,41] and Eq. (10) was widely verified by applying gas adsorption data[11,32–35], the isotherm Eqs. (10), (12), and (17) require further experimental verification and will be studied in future.

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