

# HETEROGENEOUS ADSORPTION: A FAMILY OF ISOTHERMS VIA PIECEWISE-LINEAR APPROACH

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## ABSTRACT

An inclusive model describing heterogeneous monolayer adsorption by a family of mathematical forms for overall isotherms is presented and discussed. The overall isotherms are obtained by averaging of various local isotherms, each valid for an idealised elementary homogeneous surface fragment. The local isotherm is constructed on the basis of the bottleneck principle logically completing Henry's law. Within the unifying frame of our model, the Langmuir, Toth, Volmer, Hill & de Boer, and Jovanovic isotherms are obtained as special cases of surface heterogeneity.

## INTRODUCTION

The simplest adsorption isotherm known as Henry's law [1] states that

$$\theta = Kc \quad (1)$$

where  $\theta$  ( $\leq 1$ ) is the amount adsorbed (or the surface coverage),  $c$  is the adsorbate concentration, and  $K$  is a constant. For a wide range of concentrations (or partial pressures), the form (1) perfectly describes adsorption of gases by liquid adsorbent surfaces [1, 13]. For solid surfaces, however, form (1) is considered to represent an approximation of an overall isotherm, valid in a narrow vicinity of the origin only, while, generally speaking, the derivative  $d\theta/dc$  monotonously decreases from  $K$  to 0 [12].

Modelling of heterogeneous adsorption usually stems from the depicting an adsorbent surface as a mosaic of idealised elementary homogeneous fragments, each described by a simple local isotherm [12]. An overall isotherm has then to be derived by averaging of the array of local isotherms. The rectangular hyperbola attractive by its mathematical simplicity, known as the Langmuir isotherm [2],

$$\theta = \frac{K P c}{P + K c} \quad (2)$$

was the first fundamental step towards description of heterogeneous adsorption. The form [2] produces a smooth convex curve starting in the origin with a slope equal to  $K$  and approaching plateau level  $P$  as  $c$  tending to the infinity (Fig. 1A).

There were several semi-empirical attempts to emend and extend the hyperbolic Langmuir isotherm to fit more experimental data; among them, the Toth isotherm:

$$\theta = \frac{K P c}{\left(P^n + K^n c^n\right)^{\frac{1}{n}}} \quad (3)$$

where  $n \in (0, +\infty)$  is an empirical parameter. An advantage of the form (3) is its flexibility. Obviously, at  $n = 1$ , it transforms into the Langmuir isotherm (2). At low  $n \ll 1$ , a curve generated by the form (3) creeps along the abscissa (at  $n \rightarrow 0$  it coincides with the abscissa), while at  $n \rightarrow \infty$ , it produces the Blackman type [14, 15] two-linear-pieces (piecewise-linear, slope-and-ceiling) plateau curve (Fig. 1A):

$$\theta = \min (Kc, P) \quad (4)$$

Form (4) is a natural generalisation of the Henry's law, taking into account finite capacity of an adsorbent (a maximum amount that can be adsorbed). Mathematically, it expresses the bottleneck (or piecewise-linear) principle [14, 15].

Some semi-empirical isotherms use the inverse Langmuir hyperbola

$$c = \frac{P\theta}{K(P - \theta)} \quad (2')$$

as its part, among them:

$$\text{Fowler isotherm [8-9]: } c = \frac{P\theta}{K(P - \theta)} e^{-s\theta}, \quad (5)$$

$$\text{Volmer isotherm [7]: } c = \frac{P\theta}{K(P - \theta)} e^{\frac{P\theta}{K(P-\theta)}}, \quad (6)$$

$$\text{and Hill \& de Boer isotherm [10]: } c = \frac{P\theta}{K(P - \theta)} e^{\frac{P\theta}{K(P-\theta)} - m\theta}, \quad (7)$$

where  $s$  ( $-\infty < s \leq 1$ ) and  $m$  ( $-\infty < m \leq 1/K+1/P$ ) are empirical parameters with no physical meaning (at  $s > 1$  and  $m > 1/K+1/P$ , derivative  $d\theta/dc$ , though equal to  $K$  at the origin, exceeds  $K$  at some  $c > 0$ , resulting in S-shaped curves inconsistent with Henry's law).

Having been created to satisfy particular and rather sporadic sets of experimental data, none of the forms (5) to (7) has a formidable theoretical basis. Conspicuously paying tribute to the Langmuir isotherm, they, in fact, break off with it as purely artificial experimentalists' constructions, mechanically mixing two discordant descriptions: hyperbolic and exponential. Even practically they were not an overwhelming success. Lack of their generality resulted in a comment «well-known but seldom used» pronounced about this kind of isotherms [11]. In addition, they were written as inverse functions, of the  $c = f(\theta)$  type, because the corresponding direct functions, of the  $\theta = f(c)$  type, have no simple analytical expressions (require use of the ambiguous and inconvenient Lambert function  $W$ ).

Theoretically more supportable is the Jovanovic isotherm [4-6]:

$$\theta = P \left( 1 - e^{-\frac{Kc}{P}} \right) \quad (8)$$

and its twin expression

$$\theta = Kc \left( 1 - e^{-\frac{P}{Kc}} \right) \quad (9)$$

used in neighbouring fields, among others in the mathematical biology where it is known as the Thornley curve [16]. The curve produced by form (9) goes very closely to the Fowler isotherm (5) at  $s = 1$  (see Fig. 1A) but is notably simpler to be handled and has one parameter less (at  $s = 0.8$ , the curves practically coincide).

It will be shown below that form (8) and (9) are just the top of the iceberg of a wealth of other expressions resulting from our model and combining exponent and polynomial components.

Fig. 1A compares all the above isotherms in their normalised form ( $K = 1, P = 1$ ).

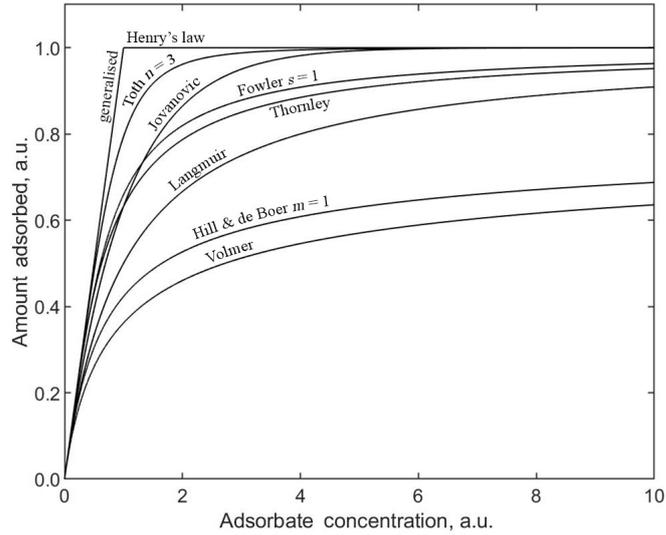


Fig. 1A. Normalised ( $K = 1, P = 1$ ) acknowledged isotherms describing heterogeneous adsorption and homogeneous adsorption (the generalised Henry's law), in arbitrary units.

In Fig. 1B, the same isotherms are depicted in the George Scatchard ( $\theta, \theta/c$ )-coordinates allowing to compare curves' shapes along the whole range of  $c \in [0 \leq c < \infty]$  and  $\theta \in [0 \leq \theta \leq P]$  in a  $1 \times 1$  square.

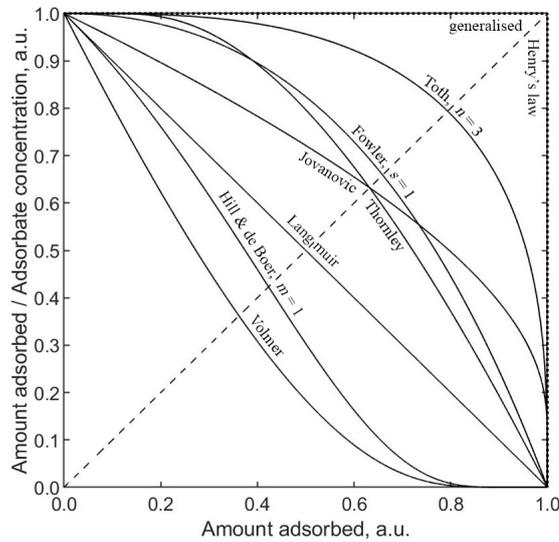


Fig. 1A. Normalised ( $K = 1, P = 1$ ) acknowledged isotherms in Scatchard ( $\theta, \theta/c$ )-coordinates describing heterogeneous adsorption (solid) and homogeneous adsorption (dotted), with  $c=1$  diagonal (dashed), in arbitrary units.

It is worth to mention that in the Scatchard coordinates, the Jovanovic isotherm is the inverse function ( $f^{-1}$ ) of the Thornley isotherm, and *vice versa* (the curves are symmetrical with respect to the diagonal  $c = 1$  ( $\theta/c = \theta$ ) of the Fig. 1B square).

#### IDEAL HOMOGENEOUS ADSORPTION: BOTTLENECK POSTULATE

For an idealised homogenous adsorbent of a small surface fragment, any lateral interaction between adsorbate and adsorbent, as well as any other environmental effects, are postulated to be negligible even near the saturation, so in our model, the idealised local isotherm strictly obeys to the generalised

piecewise-linear Henry's law (4). The function (4) may be and often has been regarded as an approximation of a phenomenologically expected smooth convex isotherm but within our model we treat it as a strict mechanistic relation for this idealised case of strict homogeneity.

#### HETEROGENEITY: MAIN ASSUMPTIONS OF THE MODEL

For the surface consisting of homogeneous fragments, each described by a local piecewise-linear isotherm (4), the overall isotherm can be calculated by averaging local isotherms.

Two types of heterogeneity may be distinguished:

(a) Homogeneous fragments may vary in adsorption energy (or critical escape velocity of an absorbed molecule), which is expressed in  $K$  (*energy heterogeneity*).

(b) They may differ, as well, in fragment surface saturation properties, which are expressed in the maximum monolayer capacity,  $P$  (*geometry heterogeneity*).

When both types of heterogeneity coexist, the model describes *complex heterogeneity*.

Assuming  $K$  and  $P$  to be random variables, all necessary properties of the adsorbent surface may be described by their joint probability density function  $f(K, P)$ . The problem is thereby reduced to the definition of mathematical expectation of (4) with a weight  $f(.,.)$ . The overall isotherm will then be described by the averaged Henry's constant,  $K$ , and by the average maximum monolayer capacity,  $P$ .

For the sake of simplicity, we assume that the adsorption energy of any chance fragment is not related to its adsorption capacity. Thus, parameters  $K$  and  $P$  are uncorrelated (independent) random variables, and their joint probability density function can be expressed as a product of individual probability density functions of both variables:

$$f(K, P) = f_1(K) f_2(P) \quad (10)$$

Now, the process of averaging is reduced to calculation of the following double integral:

$$\theta = \int_0^\infty f_2(P) \int_0^\infty f_1(K) \min(Kc, P) dK dP \quad (11)$$

The process of integration (11) can be carried out in two steps: first, with the respect to  $K$  (the inner integral), and second, with the respect to  $P$  (the outer integral). The order of integration may, of course, be reversed with the same result.

Since both parameters of the local isotherm,  $K$  and  $P$ , are essentially positive, the gamma probability density function

$$f_1(K) = \frac{\beta^\alpha}{\Gamma(\alpha)} K^{\alpha-1} e^{-\beta K} \quad (12)$$

$$f_2(P) = \frac{\xi^\nu}{\Gamma(\nu)} K^{\nu-1} e^{-\xi K} \quad (13)$$

is a natural choice for our model (Fig. 2). Here,  $\alpha$ ,  $\beta$ ,  $\nu$ , and  $\xi$  are parameters of the distribution, while  $\Gamma(.)$  is the gamma function.

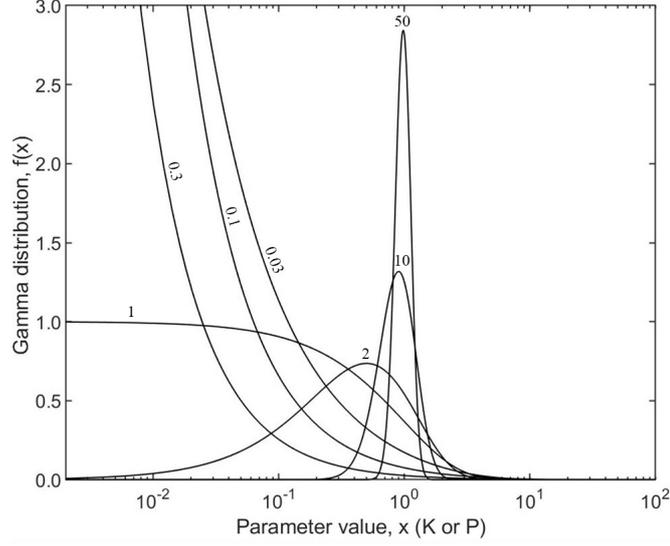


Fig. 2. Gamma probability density function in its normalised form (at  $\alpha/\beta = 1$ , or  $v/\xi = 1$ ), for  $\alpha$  (or  $v$ ) = 50, 10, 2, 1, 0.3, 0.1, 0.3.

### THE ENERGY HETEROGENEITY

Evaluating the inner integral of (11), i.e. one with respect to  $K$  (while  $P$  stays a deterministic real-valued number), one receives:

$$\theta_K = \frac{c}{\beta \Gamma(\alpha)} \gamma\left(\alpha + 1, \frac{\beta P}{c}\right) + \frac{P}{\Gamma(\alpha)} \Gamma\left(\alpha, \frac{\beta P}{c}\right), \quad (14)$$

where  $\theta_K$  is the mathematical expectation of  $\theta$ ,  $\gamma(.,.)$  is the lower incomplete gamma function, and  $\Gamma(.,.)$ , the upper incomplete gamma function.

Form (14) describe the *energy heterogeneity* (positive real-valued stochastic parameters  $\alpha$  and  $\beta$ ) combined with the *geometry homogeneity* (positive deterministic real-valued surface parameter  $P$ ). It generates a set of convex curves with first derivative  $d\theta_K/dc$  decreasing strictly monotonously from  $\alpha/\beta$  (the averaged  $K$ , or the initial slope of the isotherm) at the origin to zero at the infinity as  $\theta_K$  approaching the saturation plateau level,  $P$  (Fig. 3). Thus, the form (14) obeys Henry's law at all range of  $c \in [0, +\infty)$  and at all finite and positive real-valued ratios  $\alpha/\beta$ .

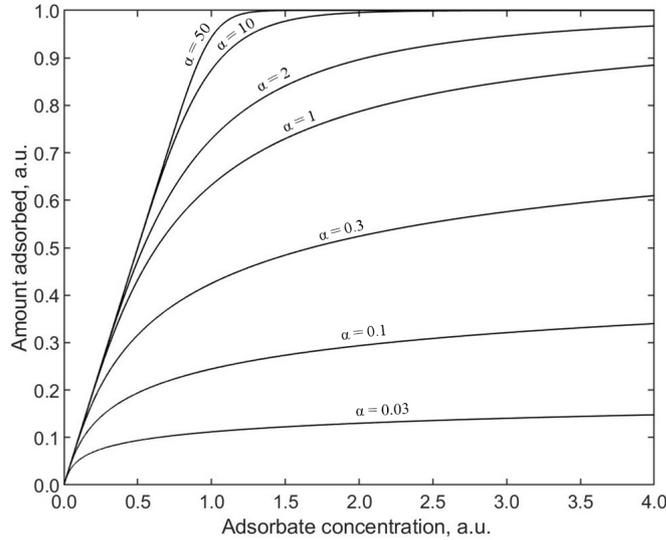


Fig. 3A. Normalised ( $\alpha/\beta = 1, P = 1$ )  $\theta_K$  isotherms (14) depicting the *energy heterogeneity*, for  $\alpha/\beta=0.03, =0.1, =0.3, =1, =2, =10, =50$ .

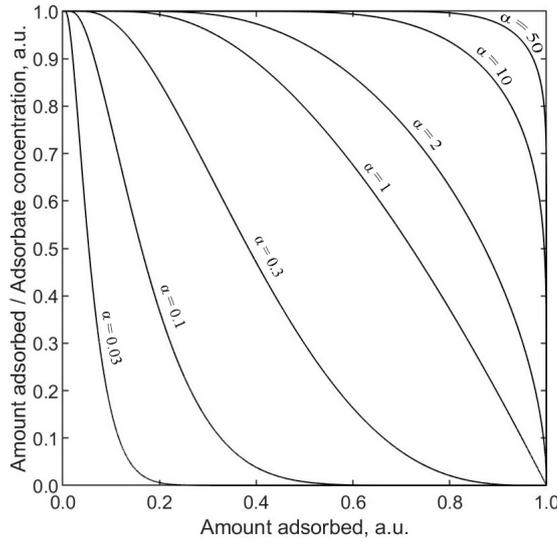


Fig. 3B. Normalised ( $\alpha/\beta = 1, P = 1$ )  $\theta_K$  isotherms (14) (the *energy heterogeneity*) in the Scatchard coordinates, for  $\alpha/\beta=0.03, =0.1, =0.3, =1, =2, =10, =50$ .

It is quite clear from the Fig. 3 that at increasing  $\alpha$ , the curves approach the initial piecewise-linear isotherm (generalised Henry's law (4)) depicting the homogeneity case. In other words, the greater  $\alpha$ , the less heterogeneous surface is (provided the ratio  $\alpha/\beta$  is constant).

At  $\alpha = 1$ , the form (14) reduces to the Thornley curve (9), with obvious substitution of  $1/\beta$  for  $K$ . It describes a special case of the pure *energy heterogeneity*, with no *geometry heterogeneity* allowed.

For five of the seven isotherms mentioned above, form (14) presents good approximations on the interval  $c \in [0, 200]$ , and nearly excellent one on the interval  $c \in [0, 20]$  (see Fig. 3). Thereby, this five curves are applicable for description of the *energy heterogeneity* of adsorption.

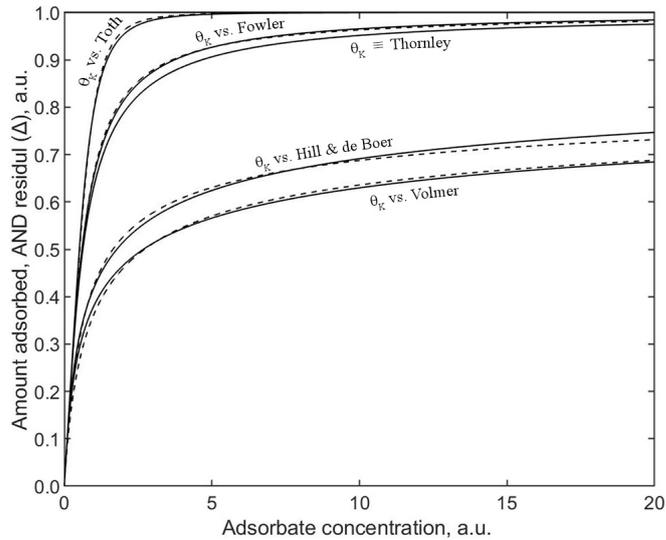


Fig. 3B. Normalised ( $\alpha = \beta, P = 1$ )  $\theta_K$  curves (solid) generated by form (14) vs. normalised ( $K = 1, P = 1$ ) known isotherms (dashed), with  $\alpha = 3.496$  ( $\theta_K$  vs. Toth's at  $n=3$ );  $\alpha = 1.152$  ( $\theta_K$  vs. Fowler's at  $s=1$ );  $\alpha = 0.233$  ( $\theta_K$  vs. Volmer's);  $\alpha=0.289$  ( $\theta_K$  vs. Hill & de Boer's with  $m=1$ ), and  $\alpha = 1$  for the Thornley isotherm which is *identical* to  $\theta_K$ .

As a comparison criterion for the curves, a residual

$$\Delta = |\theta_K - \theta_{name}| \quad (15)$$

has been chosen, with its maximum to be minimised, along with an assumption that approximation is good if  $\Delta < 3.1\% P$  on the interval of  $c \in [0, 200]$  arbitrary units. With such an assumption, the form (14) convincingly simulates the Fowler and Toth isotherms, as  $\Delta < 0.8\% P$  for the former, and  $\Delta < 1.1\% P$  for the latter (at  $n = 3$ ) for all range of  $c \in [0, \infty)$ . The approximation of the Volmer isotherm ( $\Delta < 2.4\% P$  for  $c \leq 200$  a.u.) and the Hill & de Boer isotherm ( $\Delta < 3.1\% P$  for  $c \leq 200$  a.u.), though acceptable within our frames, deteriorate with increasing  $c$ , but became totally unacceptable only at the concentration unrealistically large, of about hundred thousand and million arbitrary units (as the both isotherms goes to the plateau extremely slowly). As for the Langmuir isotherm (i.e. the Toth isotherm for  $n = 1$ ) and the Jovanovic isotherm, good approximation by the form (14) is not available at all, with the physical interpretation that these isotherms do not fit (were not constructed) to describe the *energy heterogeneity* combined with the *geometry homogeneity*. On the contrary, the Thornley isotherm, with  $\Delta \equiv 0$  for all range of  $c \in [0, \infty)$ , represents the pure special case of the *energy heterogeneity* and thus do not applicable to describe *geometry heterogeneity* (see Tab. 1).

TABLE 1  
 $\theta_K$  curves (14) vs. acknowledged isotherms,  
matching the criterion of the residual  $\Delta$  maximum minimised.

Langmuir	Toth $n = 3$	Fowler $s = 1$	Volmer	Hill & de Boer $m = 1$	Jovanovic	Thornley
$\theta_K$ $\alpha = \beta = 0.564$	$\theta_K$ $\alpha = \beta = 3.496$	$\theta_K$ $\alpha = \beta = 1.152$	$\theta_K$ $\alpha = \beta = 0.2194$	$\theta_K$ $\alpha = \beta = 0.2676$	$\theta_K$ $\alpha = \beta = 1.298$	$\theta_K$ $\alpha = \beta = 1$
$\Delta \leq 0.04994$ on $c \in [0, +\infty)$ . $\Delta$ reaches its max of 0.04994 at $c=0.5423$ .  $\Delta > 3.1\% P$ at low $c$ . Not acceptable.	$\Delta \leq 0.010259$ on $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.010259 at $c=1.564$ .  $\Delta < 1.1\% P$ for any $c$ . Good.	$\Delta \leq 0.007852$ on $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.007852 at $c=0.3794$ .  $\Delta \leq 0.8\% P$ for any $c$ . Good.	$\Delta \leq 0.02335$ on $c \in [0, 200]$ , reaching its local extremes at $c=0.297$ and 10,5186. $\Delta < 0.031$ until $c=4458$ and reaches its global max of 0.05028 at $c=4,602,037$ .  Acceptable as $\Delta < 2.4\% P$ on $c \in [0, 200]$ .	$\Delta \leq 0.03004$ on $c \in [0, 200]$ reaching its local minimum of -0.03003 at $c = 2.784$ . $\Delta = +0.0300$ at $c=200$ and reaches its global max of 0.06183 at $c=115,694$ .  Acceptable as $\Delta < 3.1\% P$ on $c \in [0, 200]$ .	$\Delta \leq 0.059262$ at $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.0592061 at $c=3.5480$ .  $\Delta > 3.1\% P$ at low $c$ . Not acceptable.	$\Delta = 0$ on $c \in [0, +\infty)$ .  Curves are identical.

In addition to the  $\theta_K$  at  $\alpha = 1$ , i.e. to the Thornley curve which takes the form

$$\theta_K = \frac{c}{\beta} \left( 1 - e^{-\frac{\beta P}{c}} \right) \quad (9)$$

two other formulae following from (14) at  $\alpha = 2$  and 3 may turn out to be simple and ostensive instruments for description of the *energy heterogeneity*:

$$\theta_K = \frac{2c}{\beta} \left( 1 - e^{-\frac{\beta N}{c}} \left( 1 + \frac{1}{2} \frac{\beta N}{c} \right) \right) \quad (16)$$

$$\theta_K = \frac{3c}{\beta} \left( 1 - e^{-\frac{\beta N}{c}} \left( 1 + \frac{2}{3} \frac{\beta N}{c} + \frac{1}{6} \frac{\beta^2 N^2}{c^2} \right) \right) \quad (17)$$

In general, at any integer  $\alpha \geq 1$  and any real-valued  $\beta > 0$ , expression (14) takes the following form:

$$\theta_K = \frac{\alpha c}{\beta} \left( 1 - e^{-\frac{\beta P}{c}} \sum_{i=0}^{\alpha-1} \left( 1 - \frac{i}{\alpha} \right) \frac{\left( \frac{\beta P}{c} \right)^i}{i!} \right) \quad (18)$$

### THE GEOMETRY HETEROGENEITY

Changing the order of integration in (11) and evaluating the integral with respect to  $P$  (while  $K$  stays a deterministic real-valued number), one receives:

$$\theta_P = \frac{1}{\xi \Gamma(\nu)} \gamma(\nu + 1, \xi K c) + \frac{K c}{\Gamma(\nu)} \Gamma(\nu, \xi K c) \quad (19)$$

Form (19) describe the *geometry heterogeneity* (positive real-valued stochastic parameters  $\nu$  and  $\xi$ ) combined with the *energy homogeneity* (positive deterministic real-valued surface parameter  $K$ ). Expression (19) obeys Henry's law at all range of  $c \in [0, +\infty)$  and at all finite and positive real-valued ratios  $\nu/\xi$ . It generates a family of convex curves (Fig. 4) with first derivative  $d\theta_P/dc$  decreasing strictly monotonously from  $K$  at the origin to zero at the infinity, as  $\theta_P$  approaching the saturation plateau level of the isotherm,  $\nu/\xi$  (the averaged  $P$ ).

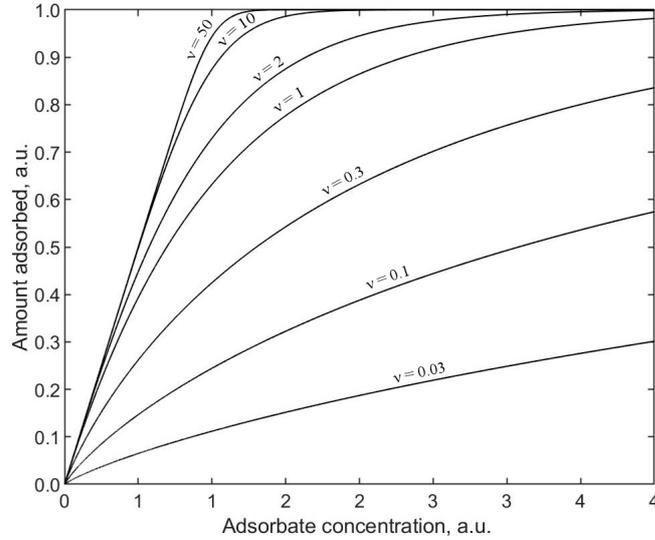


Fig. \$A. Normalised ( $K = 1, \nu/\xi = 1$ )  $\theta_P$  isotherms (19) depicting the *geometry heterogeneity*, for  $\nu=0.03, =0.1, =0.3, =1, =2, =10, =50$ .

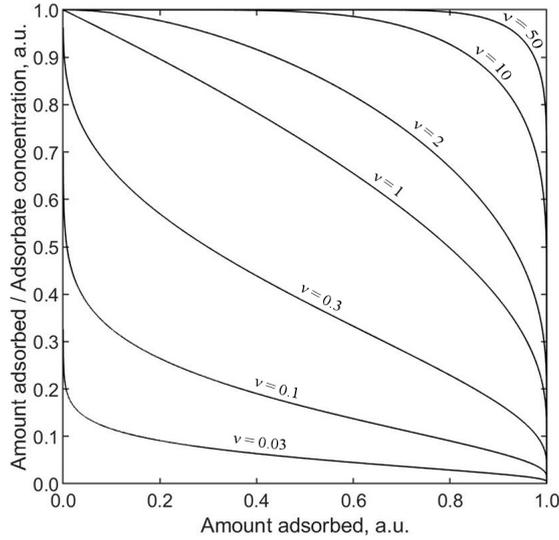


Fig. 4B. Normalised ( $K = 1, v/\xi = 1$ )  $\theta_K$  isotherms (19) (the *geometry heterogeneity*) in the Scatchard coordinates, for  $v=0.03, =0.1, =0.3, =1, =2, =10, =50$ .

It is quite clear from the Fig. 4 that at increasing  $v$ , the curves approach the initial piecewise-linear isotherm (generalised Henry's law (4)) depicting the homogeneity case. In other words, the greater  $v$ , the less heterogeneous surface is (provided the ratio  $v/\xi$  is constant).

At  $v = 1$ , the Jovanovic isotherm immediately follow from (19), with the obvious substitution of  $1/\xi$  for  $P$ . Thus, the Jovanovic isotherm represents the pure special case of the *geometry heterogeneity* and not applicable to description of the *energy heterogeneity*. Apart from it, only the Toth isotherm out of the seven acknowledged isotherms discussed above can be reasonably simulated by the form (19) under the above criterion (see Tab. 2). It means that the others six isotherms were not constructed for depicting the *geometry heterogeneity*.

TABLE 2  
 $\theta_P$  curves (19) vs. acknowledged isotherms,  
matching the criterion of the residual  $\Delta$  maximum minimised.

Langmuir	Toth $n = 3$	Fowler $s = 1$	Volmer	Hill & de Boer $m = 1$	Jovanovic	Thornley
$\theta_P$ $v = \xi = 0.30576$	$\theta_P$ $v = \xi = 3.1865$	$\theta_P$ $v = \xi = 0.85458$	$\theta_P$ $v = \xi = 0.0419125$	$\theta_P$ $v = \xi = 0.0735025$	$\theta_P$ $v = \xi = 1$	$\theta_P$ $v = \xi = 0.711867$
$\Delta \leq 0.075062$ on $c \in [0, +\infty)$ . $\Delta$ reaches its max of 0.075062 at $c = 0.76185$ .	$\Delta \leq 0.014568$ on $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.014568 at $c = 0.79845$ .	$\Delta \leq 0.064443$ on $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.064443 at $c = 0.68554$ .	$\Delta \leq 0.2305626$ on $c \in [0, +\infty)$ , reaching its max of 0.230563 at $c = 1.5589$ .	$\Delta \leq 0.220959$ on $c \in [0, +\infty)$ reaching its max of 0.220959 at $c = 1.1456$ .	$\Delta = 0$ on $c \in [0, +\infty)$ . Curves are identical.	$\Delta \leq 0.07526396$ at $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.07526396 at $c = 0.60490$ .
$\Delta \geq 3.1\%$ at low $c$ . Not acceptable.	$\Delta < 1.5\%$ for any $c$ . Good.	$\Delta > 3.1\%$ at low $c$ . Not acceptable.	$\Delta \geq 3.1\%$ at low $c$ . Not acceptable.	$\Delta \geq 3.1\%$ at low $c$ . Not acceptable.		$\Delta \geq 3.1\%$ at low $c$ . Not acceptable.

In addition to the Jovanovic isotherm (i.e. to  $\theta_P$  at  $v = 1$ ) which takes the form

$$\theta_P = \frac{1}{\xi} \left( 1 - e^{-K\xi c} \right) \quad (8')$$

two other formulae following from (19) at  $v = 2$  and 3 may turn out to be simple and ostensive instruments for description of the *geometry heterogeneity*:

$$\theta_P = \frac{2}{\xi} \left( 1 - e^{-K\xi c} \left( 1 + \frac{1}{2} K\xi c \right) \right) \quad (20)$$

$$\theta_P = \frac{3}{\xi} \left( 1 - e^{-K\xi c} \left( 1 + \frac{2}{3} K\xi c + \frac{1}{3} K^2 \xi^2 c^2 \right) \right) \quad (21)$$

In general, at any integer  $\nu \geq 1$  and any real-valued  $\xi > 0$ , expression (19) takes the following form :

$$\theta_P = \frac{\nu}{\xi} \left( 1 - e^{-K\xi c} \sum_{i=0}^{\nu-1} \left( 1 - \frac{i}{\nu} \right) \frac{(K\xi c)^i}{i!} \right) \quad (22)$$

### THE COMPLEX HETEROGENEITY

Using forms (14) and (19), the double integral (11) for the mathematical expectation of the amount adsorbed in its most general form may be re-written as :

$$\theta_{KP} = \int_0^{\infty} \theta_K f_2(P) dP \quad (23)$$

where  $\theta_K$  is defined by (14) and  $f_2(P)$  by (13); or, with reversing integration order, as

$$\theta_{PK} = \int_0^{\infty} \theta_P f_1(K) dK \quad (24)$$

where  $\theta_P$  is defined by (19) and  $f_1(K)$  by (12). Obviously,  $\theta_{KP} \equiv \theta_{PK}$  because they differ by the order of integration only. It's also worth to mention that  $\theta_{KP} \rightarrow \theta_K$  at  $\nu/\xi$  constant and  $\nu \rightarrow \infty$ , while  $\theta_{PK} \rightarrow \theta_P$  at  $\alpha/\beta$  constant and  $\alpha \rightarrow \infty$ , the result following from the fact that the gamma distribution function degenerates into the Dirac delta function as its variance tends to the infinity.

Form (23) (or (24)) describes the *complex heterogeneity* (the *energy heterogeneity* combined with the *geometry heterogeneity*). Each set of curves obeys Henry's law at all range of  $c \in [0, +\infty)$  and all finite and positive real-valued parameters  $\alpha$ ,  $\beta$ ,  $\nu$ , and  $\xi$  each one generates a family of convex curves with first derivatives  $d\theta_{PK}/dc$  and  $d\theta_{KP}/dc$  decreasing strictly monotonously from  $\alpha/\beta$  (the averaged  $K$ ) at the origin to zero at the infinity as the isotherms approach the saturation plateau level  $\nu/\xi$  (the averaged  $P$ ) (see Fig. 5A and Fig. 5B).

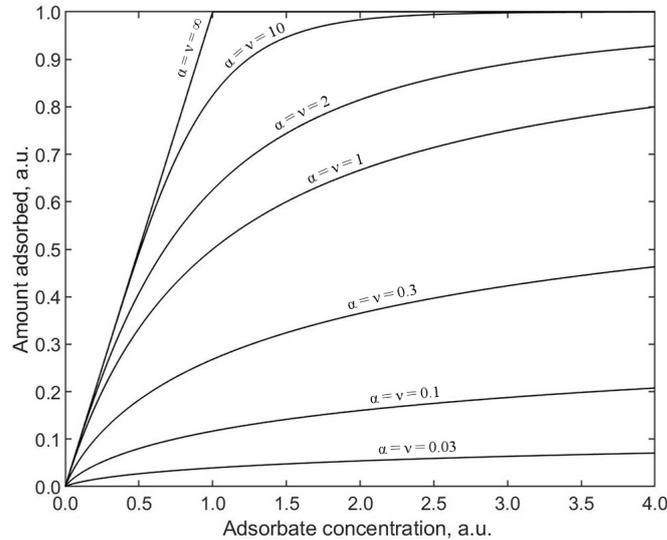


Fig. 5A. Normalised ( $\alpha/\beta = 1, v/\xi = 1$ )  $\theta_{KP/PK}$  isotherms (23) (or (24)) depicting the *complex heterogeneity*, for switching  $\alpha = v=0.03, =0.1, =0.3, =1, =2, =10, =\infty$ .

At  $\alpha = v = 1$ , the normalised Langmuir isotherm immediately follows from (23) (or (24)):

$$\theta_{KP} \equiv \theta_{PK} = \frac{c}{\beta + \xi c} \quad (25)$$

Expression (25) formulates the simplest possible special case of the *complex heterogeneity*, with the *energy heterogeneity* and the *geometry heterogeneity* represented in equal shares. On Fig. 5B, the corresponding line makes the main diagonal of the Scatchard square.

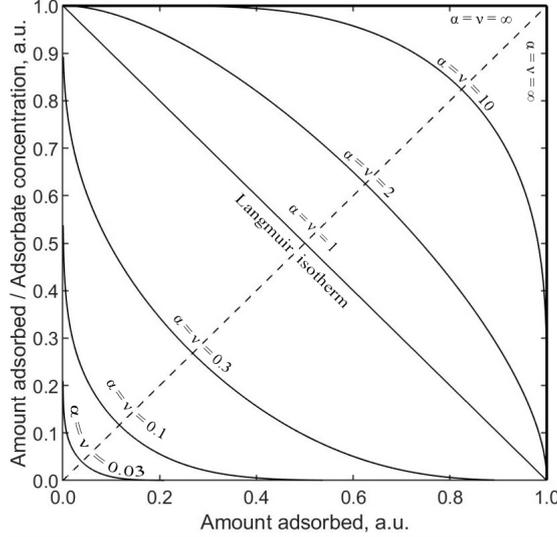


Fig. 5B. Normalised ( $\alpha/\beta = 1, v/\xi = 1$ )  $\theta_{KP/PK}$  isotherms (23) (or (24)) depicting the *complex heterogeneity*, in Scatchard coordinates, the *energy* and *geometry heterogeneity* represented in equal shares, for  $\alpha=v=0.03, =0.1, =0.3, =1, =2, =10, =\infty$  (bold).

All isotherms plotted on the Fig. 5B are symmetrical with respect of the diagonal  $c = 1$  (dashed) because  $\alpha = v$ , i. e. the *energy heterogeneity* and *geometry heterogeneity* are represented in equal shares.

At  $\alpha = \beta \rightarrow \infty$  and  $v = \xi \rightarrow \infty$ , the stochastic model set by (23) (or (25)) regenerates into initial deterministic one, i.e. into normalised generalised Henry's law (4):

$$\theta_{KP} \equiv \theta_{PK} = \min(x, 1) \quad (26)$$

In form (26), the stochastic model elaborated above degenerates into the initial deterministic one. In other words, (26) formulates the simplest special case of the normalised *total homogeneity*, as it has been embodied into the basis of our model.

Some typical  $\theta_{KP/PK}$  isotherms for  $\alpha$  not necessarily equal to  $v$  are shown on Fig. 5C and Fig. 5D in the Scatchard coordinates. The main diagonal of the Scatchard square separates zones where either the *energy heterogeneity*, or the *geometry heterogeneity* prevails.

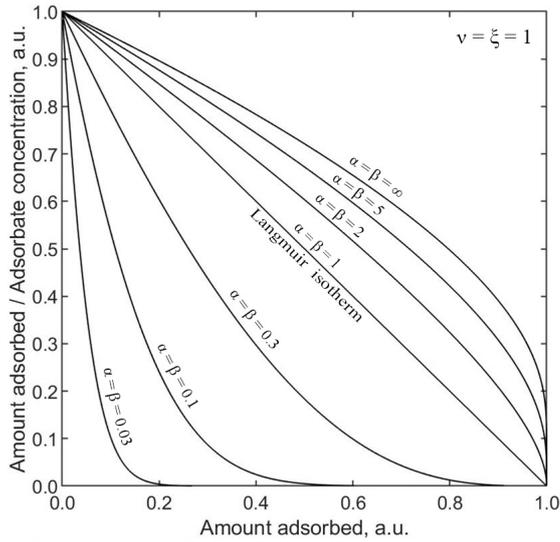


Fig. 5C. Normalised ( $\alpha/\beta = 1, v/\xi = 1$ )  $\theta_{KP/PK}$  isotherms (23) (or (24)) depicting the *complex heterogeneity*, in Scatchard coordinates, for  $v = 1$ , and  $\alpha=0.03, =0.1, =0.3, =1, =2, =5, =\infty$ . For curves lying above the Langmuir isotherm ( $\alpha > v$ ), the *geometry heterogeneity* prevails, while for curves below the Langmuir isotherm, the *energy heterogeneity* prevails.

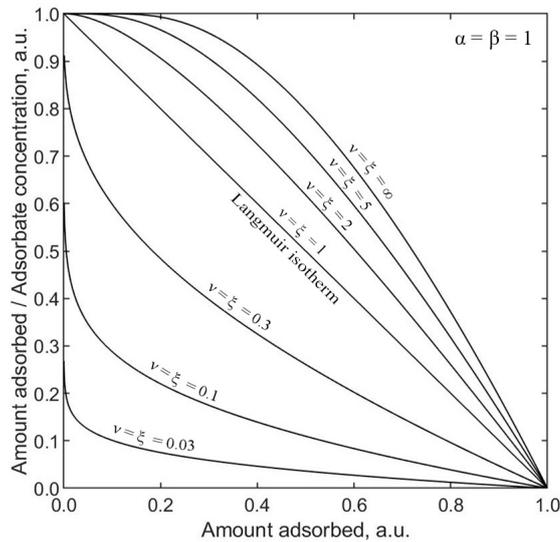


Fig. 5D. Normalised ( $\alpha/\beta = 1, v/\xi = 1$ )  $\theta_{KP/PK}$  isotherms (23) (or (24)) depicting the *complex heterogeneity*, in Scatchard coordinates, for  $\alpha = 1$ , and  $v=0.03, =0.1, =0.3, =1, =2, =5, =\infty$ . For curves lying above the Langmuir isotherm ( $\alpha < v$ ), the *energy heterogeneity* prevails, while for curves below the Langmuir isotherm, the *geometry heterogeneity* prevails.

It is worth to mention that in the Scatchard coordinates, any  $\theta_{KP/PK}(\alpha, \beta, v, \xi)$  isotherm, for any fixed parameters  $\alpha, \beta, v, \xi$ , is the inverse function ( $f^{-1}$ ) of the  $\theta_{KP/PK}(v, \xi, \alpha, \beta)$  isotherm, and *vice versa* (the curves are symmetrical with respect to the diagonal  $c = 1$  ( $\theta/c = \theta$ ), see Fig. 5E square).

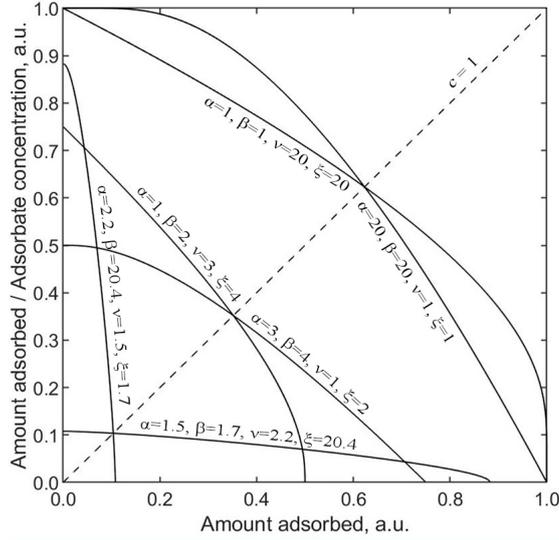


Fig. 5E. An example of the twin  $\theta_{KP/PK}$  isotherms' symmetry, in Scatchard coordinates:  
 1st pair:  $\alpha = 1, \beta = 1, \nu = 20, \xi = 20$   
 vs.  $\alpha = 20, \beta = 20, \nu = 1, \xi = 1$   
 2nd pair:  $\alpha = 1, \beta = 2, \nu = 3, \xi = 4$   
 vs.  $\alpha = 3, \beta = 4, \nu = 1, \xi = 2$ ;  
 3rd pair:  $\alpha = 1.5, \beta = 1.7, \nu = 2.2, \xi = 20.4$   
 vs.  $\alpha = 2.2, \beta = 20.4, \nu = 1.5, \xi = 1.7$ ;

Table 3 puts into comparison  $\theta_{KP/PK}$  isotherms (23) (or (24)) against the acknowledged isotherms discussed above.

TABLE 3  
 $\theta_{KP/PK}$  curves (24) or (25) vs. acknowledged isotherms,  
 matching the criterion of the residual  $\Delta$  maximum minimised.

Langmuir	Toth $n = 3$	Fowler $s = 1$	Volmer	Hill & de Boer, $m = 1$	Jovanovic	Thornley
$\theta_{KP/PK}$ $\alpha = \beta = 1$ $\nu = \xi = 1$	$\theta_{KP/PK}$ $\alpha = \beta = 6.9023$ $\nu = \xi = 6.9023$	$\theta_{KP/PK}$ $\alpha = \beta = 1.2287$ $\nu = \xi = 21.5$	$\theta_{KP/PK}$ $\alpha = \beta = 0.2194$ $\nu = \xi \rightarrow \infty$	$\theta_{KP/PK}$ $\alpha = \beta = 0.2679$ $\nu = \xi \rightarrow \infty$	$\theta_{KP/PK}$ $\alpha = \beta \rightarrow \infty$ $\nu = \xi = 1$	$\theta_{KP/PK}$ $\alpha = \beta \rightarrow \infty$ $\nu = \xi = 1$
$\Delta \equiv 0$ on $c \in [0, +\infty)$ .  Curves are identical. Ideal.	$\Delta \leq 0.004638$ on $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.014568 at $c = 1.0361$ .  $\Delta < 0.5\%$ for any $c$ . Excellent.	$\Delta \leq 0.0059324$ on $c \in [0, +\infty)$ . $\Delta$ reached its max of 0.0059324 at $c = 0.35447$ .  $\Delta < 0.6\%$ for any $c$ . Excellent.	$\Delta \leq 0.02335$ on $c \in [0, 200]$ , as $\theta_{KP/PK} \rightarrow \theta_K$ .  Acceptable as $\Delta < 2.4\%$ on $c \in [0, 200]$ .	$\Delta \leq 0.03003$ on $c \in [0, 200]$ , as $\theta_{KP/PK} \rightarrow \theta_K$ . Acceptable as $\Delta < 31\%$ on $c \in [0, 200]$ .	$\Delta \equiv 0$ on $c \in [0, +\infty)$ . as $\theta_{KP/PK} \rightarrow \theta_P$ .  Curves are identical. Ideal.	$\Delta \equiv 0$ on $c \in [0, +\infty)$ . as $\theta_{KP/PK} \rightarrow \theta_K$ .  Curves are identical. Ideal.

It is clear from the Tab. 3 that the Toth isotherm, as far as the Langmuir one, represent the *energy heterogeneity* and the *geometry heterogeneity* in equal shares, while the Fowler isotherm describes rather the *energy heterogeneity* than the *geometry heterogeneity*. The general rule for comparison appearing from our stochastic model reads as follows: at fixed ratios  $\alpha/\beta$  and  $\nu/\xi$ ,  $\alpha < \nu$  means that the *energy heterogeneity* prevails, while at  $\alpha > \nu$ , the *geometry heterogeneity* prevails. As an illustration, consider  $\theta_K$  and  $\theta_P$  vs. the Fowler isotherm. It's clear from Table 1 and Table 2 that  $\theta_K$  (the *energy heterogeneity*) is closer to the Fowler isotherm than  $\theta_P$  (the *geometry heterogeneity*); and from Table 3,

$\alpha = 1.2287 < \nu = 21.5$  reads as the *energy heterogeneity* prevails. At the limiting case of no the *energy heterogeneity*,  $\nu \rightarrow \infty$ ; while in absence of the *geometry heterogeneity*,  $\alpha \rightarrow \infty$ .

In addition to the normalised Langmuir isotherm as  $\theta_{KP/PK}$  (25), three other hyperbolic formulae, following from (23) at  $\alpha = 1, = 2$ , and  $= 3$  with  $\beta, \nu$ , and  $\xi$  real-valued, may turn out to be simple and ostensive instruments for description of the *complex heterogeneity*:

$$\theta_{KP} = \frac{c}{\beta} \left( 1 - \frac{\xi^\nu}{\left(\xi + \frac{\beta}{c}\right)^\nu} \right) \quad (27)$$

$$\theta_{KP} = \frac{2c}{\beta} \left( 1 - \frac{\xi^\nu}{\left(\xi + \frac{\beta}{c}\right)^\nu} - \frac{1}{2} \frac{\beta}{c} \frac{\xi^\nu \nu}{\left(\xi + \frac{\beta}{c}\right)^{\nu+1}} \right) \quad (28)$$

$$\theta_{KP} = \frac{3c}{\beta} \left( 1 - \frac{\xi^\nu}{\left(\xi + \frac{\beta}{c}\right)^\nu} - \frac{2}{3} \frac{\beta}{c} \frac{\xi^\nu \nu}{\left(\xi + \frac{\beta}{c}\right)^{\nu+1}} - \frac{1}{3} \frac{\beta^2}{c^2} \frac{\xi^\nu (\nu + 1) \nu}{\left(\xi + \frac{\beta}{c}\right)^{\nu+2}} \right) \quad (29)$$

In general, at any integer positive  $\alpha$  and any real-valued positive  $\beta, \nu$ , and  $\xi$ , expression (23) takes the following form:

$$\theta_{KP} = \frac{\alpha c}{\beta} \left( 1 - \frac{\xi^\nu}{(\nu - 1)!} \sum_{i=0}^{\alpha-1} \left( 1 - \frac{i}{\alpha} \right) \frac{(\nu + i - 1)!}{i!} \frac{\left(\frac{\beta}{c}\right)^i}{\left(\xi + \frac{\beta}{c}\right)^{\nu+i}} \right) \quad (30)$$

Similarly, three other hyperbolic formulae, following from (24) at  $\nu = 1, = 2$ , and  $= 3$ , may be add to the library of simple and ostensive analytical experimentalists' tools for description of the *complex heterogeneity*:

$$\theta_{PK} = \frac{1}{\xi} \left( 1 - \frac{\beta^\alpha}{(\beta + \xi c)^\alpha} \right) \quad (31)$$

$$\theta_{PK} = \frac{2}{\xi} \left( 1 - \frac{\beta^\alpha}{(\beta + \xi c)^\alpha} \left( 1 + \frac{1}{2} \frac{\alpha \xi c}{\beta + \xi c} \right) \right) \quad (32)$$

$$\theta_{PK} = \frac{3}{\xi} \left( 1 - \frac{\beta^\alpha}{(\beta + \xi c)^\alpha} \left( 1 + \frac{2}{3} \frac{\alpha \xi c}{\beta + \xi c} + \frac{1}{3} \frac{(\alpha + 1) \alpha \xi^2 c^2}{(\beta + \xi c)^2} \right) \right) \quad (33)$$

In general, at any integer  $\nu \geq 1$  and any real-valued positive  $\alpha, \beta$ , and  $\xi$ , expression (24) takes the following form:

$$\theta_{PK} = \frac{\nu}{\xi} \left( 1 - \frac{\beta^\alpha}{(\alpha - 1)!} \sum_{i=0}^{\nu-1} \left( 1 - \frac{i}{\nu} \right) \frac{(\alpha + i - 1)!}{(i)!} \frac{(\xi c)^i}{(\beta + \xi c)^{\alpha+i}} \right) \quad (34)$$

## DISCUSSION AND CONCLUSION

It has been demonstrated by the above graphs and calculations that our model encloses all the acknowledged isotherms as its special cases and theoretically substantiates them. In addition, it gives a wealth of extra isotherms constructed on the same theoretical basis. The flexibility of the model seems also to have been made obvious.

The model explicitly distinguish two kinds of the heterogeneity: the *energy* one linked to the initial slope of the isotherms, and the *geometry* one coupled with the capacity of any adsorbent fragment. It has been shown that a shape of an experimental curve can in advance, before any physical and chemical analysis of the adsorbent surface, say a lot about what kind of heterogeneity prevails.

The acknowledged isotherms discussed above (the Langmuir, Toth, Fowler Volmer, Hill & de Boer, Jovanovic, and Thornley) are all either two-parameter or three-parameter ones, while the stochastic approach model presented here results in either three-parameter ( $\theta_K$  and  $\theta_P$ ) or, in its main part, in four-parameters ( $\theta_{KP}$  and  $\theta_{PK}$ ) ones. However the four parameter set doesn't seem to be a drastic disadvantage. In practice, experimentalists will never deal with parameters  $\alpha$ ,  $\beta$ ,  $\nu$ , and  $\xi$  themselves but rather with get their ratios: the initial slope  $\alpha/\beta$  and the plateau level  $\nu/\xi$ . Thus, all the  $\theta_K$ ,  $\theta_P$ ,  $\theta_{KP}$ , and  $\theta_{PK}$  curves became two-parameter ones. And they have a *practical* strength over the acknowledged isotherms (to say nothing about their *theoretical* advantage) because, while ratios the  $\alpha/\beta$  and  $\nu/\xi$  stay constant, the varying of  $\alpha$  or  $\nu$ , as it was shown above, widely controls the shape of a curve.

Nor the equations with gamma functions and integrals should be nowadays considered as too problematic when the statistical data handling is in question. But if, for any reason, simple formulae are preferable, the ostensive algebraic expressions (27) to (34) presented above may be effortlessly used, and it doesn't seem to be a strict constraint that  $\alpha$  and  $\nu$  are integer, because, as it has been mentioned, it is the ratios  $\alpha/\beta$  and  $\nu/\xi$  what are the practically meaningful parameters, so, with  $\beta$  and  $\xi$  *real-valued*, these ratios may have any *real* value, too.

We get an additional degree of practical freedom, having in hand two methods of writing *identical* but seemingly different formulae. For instance, let  $\alpha = 5$ ,  $\beta = 3$ ,  $\nu = 2$ , and  $\lambda = \xi$ . It is not immediately obvious that instead of an awkward and obscure six-component formula

$$\theta_{KP} = \frac{5c}{3} \left( 1 - \frac{1}{(1 + \frac{1}{c})^2} - \frac{8}{5} \frac{1}{c(1 + \frac{1}{c})^3} - \frac{9}{5} \frac{1}{c^2(1 + \frac{1}{c})^4} - \frac{8}{5} \frac{1}{c^3(1 + \frac{1}{c})^5} - \frac{1}{c^4(1 + \frac{1}{c})^6} \right) \quad (35)$$

that follows from (30), an *identical* but simpler and more compact three-component one following from (34) is at hand:

$$\theta_{PK} = \frac{2}{3} \left( 1 - \frac{1}{(1 + \frac{1}{c})^5} - \frac{5}{2} \frac{c}{c(1 + \frac{1}{c})^6} \right) \quad (36)$$

The above critique of the gauche Lambert-type Fowler, Volmer and Hill & de Boer isotherms may be considered as important part of the work presented. These formulae was never properly examined. The inequality  $m > 1/K + 1/P$  defining domain where the Hill & and de Boer isotherm losses it physical sense is a new result.

The approach developed here may have some implementation beyond the adsorption theory and practice. In agriculture and chemistry, the bottle-neck principle has been known since the 19th century as Justus von Liebig principle [17]. A lot of processes, where a number of heterogeneous small units are to be saturated, may presumably be described by the same formalism. Assembly-line processes are also open to discussion which may lead to implementation of our model in technology and economics.

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