The Grand Ensemble of Subsystems: Applications to Fitting Single-Component Adsorption Data

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Abstract

In this work, it is reviewed the cell model of adsorption by using the small system grand ensemble method. Under the common assumption that the adsorbate phase is divided into identical and weakly-interacting subsystems, it is suggested that the general multiparametric isotherm that arise from the theory may be used to fit the experimental data of adsorption of gases and vapours on microporous adsorbents (type I isotherm), even though these present heterogeneity like pore size distribution. A simplified isotherm that reduces the number of adjustable parameters with respect to the general isotherm is proposed. Both isotherms, due to their relative high accuracy, can be used to estimate thermodynamical properties like isosteric and differential heats of adsorption. Also, a simple method is presented for systems that show an apparent variation in the coverage limit as function of temperature; for several systems, this method reduces the fitting deviations. Finally, several applications to fitting data of adsorption, taken from literature, of some gases on activated carbon, molecular sieving carbon, silica gel, and pillared clays are presented.

1 Introduction

Correlating adsorption data obtained from experiments or computer calculations is necessary to save time and efforts in additional experimentation or computing time. Because of the complexity of equilibrium adsorption phenomenon, even today, the research of new models of adsorption is active. A good parameter-adjustable model must fit well the experimental data and correctly predict thermodynamic quantities; therefore, it is necessary to analyze the model and assess its capabilities. Many real-world applications of adsorption encompass a range of saturation up to $10^6$ and $10^{12}$ in pressure [1]. Therefore, in some cases, in order to fit the adsorption data, it may be necessary models that give experimentalist and process engineer the possibility to set the number of adjustable parameters.

Many adsorbents used in industry and research present a certain degree of heterogeneity in terms of a pore size distribution and certain surface topography. Depending on each of these factors, different isotherm models are proposed. For example, lattice gas theories that simplify the structure of the adsorbent surface by taking into account the most important adsorption sites of the adsorbent surface or adsorption pores have been developed, and most of these theories are consistent with experiments and computer simulations [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. A disadvantage of this kind of models is that many gas-solid systems present unique characteristics that must be considered in each particular model. Therefore, once a model has been developed for a certain gas-solid system it must be tested with adsorption and thermodynamic data.

Another commonly used method to obtain isotherms for heterogeneous systems is the integration over a patchwise topology of adsorption sites [13]. Modified isotherms arise by assuming an adsorption energy distribution function and an ideal local isotherm like Langmuir. Nevertheless, although some of these equations work well for a large number of systems, they present limitations involved in using a particular model, e.g., some models do not provide the correct Henry’s law limit. Additionally, this method is somewhat difficult because the complexity of the adsorption energy distribution makes it difficult to obtain an analytical expression for the transformed isotherm. The Sips[14], Toth[15], and UNILAN[16] isotherms are the most widely used isotherms of this type.

Recently, a method proposed by Reiss and Merry [17] to study the small system grand ensemble (SSGE)[17, 18, 19, 20] has been useful to analyze the properties of these small subsystems that all together form a homogeneous phase. Initially, this model was proposed to study rigid spheres, but, in principle, it can be applied to other systems [19], as shown in this work for the adsorption case. The advantage of this SSGE method is
that it can be studied the implications of assuming interactions between a particular subsystem and its surroundings, allowing us to analyze in detail the properties of these small systems and their consequences for the adsorption of gases.

In this work, it is briefly reviewed the statistical mechanical cell model of adsorption [21, 22, 23] by using the SSGE method. The general isotherm that arises from the cell model has been useful to fit experimental data of adsorption of gases on zeolites [24, 25, 26, 27, 28, 29, 30, 31]. Here, an accurate and simplified isotherm is proposed, this isotherm is similar to the empirical isotherm proposed by Ruthven [32]. It is shown that both the simplified and general isotherms might be applied to the adsorption of gases on heterogeneous microporous adsorbents. To prove this hypothesis, several experimental adsorption isotherms are correctly fitted by using the isotherm equations studied here. From the fitting results, it is suggested that the isotherm equations treated here can be used to fit type I experimental adsorption isotherms and predict thermodynamic properties. Furthermore, extrapolations to temperatures near the experimental temperature range are possible. Because of the complexity of heterogeneous adsorbents, it is argued that the method presented here is semi-empirical and the cells ensemble can be considered as an abstract and idealized grand ensemble of small subsystems.

2 Theory

2.1 The General Adsorption Isotherm

Consider a single-component gas in equilibrium with an adsorbate phase. Suppose that the adsorbate phase can be divided into M identical cells that weakly interact between each other. The total number of cells is temperature-independent and the cell volume as well. Now, let us regard a particular cell as a subsystem of interest and the remaining M − 1 cells that surround this subsystem as a bath. It is assumed that the effect of the adsorbent on the adsorbate manifests only by means of an interaction potential and the adsorbate presence on the adsorbent surface (or cavities) does not affect its properties. Define the following partition functions:

\[ Q'(T,V) = \frac{1}{\Lambda^{N!}} \int_{V} d\mathbf{R}_{1} \cdots d\mathbf{R}_{N} \exp \left[ -\frac{\mathcal{V}(\mathbf{R})}{k_{B}T} \right] \]

\[ Q(T,V,N) = \frac{1}{\Lambda^{N!}} \int_{V} d\mathbf{R}_{1} \cdots d\mathbf{R}_{N} \exp \left[ -\frac{\mathcal{V}(\mathbf{R})}{k_{B}T} \right] = \frac{Z(T,V,N)}{\Lambda^{N!}} \] (2)

where \( \Lambda \) is the deBroglie thermal wavelength, V and N are the adsorbate phase volume (or area) and the total number of adsorbed molecules, respectively, \( v_{s} \) and \( n \) are the volume (or area) and number of molecules of the subsystem, respectively, and \( d \) is the adsorbate phase dimension. The potential energy \( \mathcal{V} \) may be decomposed into three contributions:

\[ \mathcal{V}(\mathbf{R}) = \mathcal{V}_{s}(\mathbf{R}_{1}, \ldots, \mathbf{R}_{n}) + \mathcal{V}_{b}(\mathbf{R}_{n+1}, \ldots, \mathbf{R}_{N}) + \mathcal{V}_{i}(\mathbf{R}) \] (3)

the term \( \mathcal{V}_{s} \) is the potential energy of a subsystem and \( \mathcal{V}_{b} \) is the bath potential energy, these potentials are the sum of the molecule-molecule and the molecule-solid interaction potentials. The term \( \mathcal{V}_{i} \) represents the interaction between the subsystem and the bath. Consider the usual probability density for the canonical ensemble [23, 33]:

\[ \rho(\mathbf{P}, \mathbf{R}) = \frac{1}{Z} \exp \left[ -\frac{\mathcal{H}(\mathbf{P}, \mathbf{R})}{k_{B}T} \right] \]

where \( C \) is a constant. If we integrate over the subsystem’s phase space and the bath’s phase space, we obtain the probability of finding \( n \) molecules in the subsystem volume \( v_{s} \) and \( N - n \) molecules in the bath volume \( V - v_{s} \):

\[ p_{n} = C \times Q'(T,V-v_{s},N-n,v_{s},n) \]

(5)

It is plausible to assume that a maximum of \( n_{s} \) molecules can adsorb on the subsystem (the adsorbent has a saturation limit). Therefore, in order to eliminate the arbitrary constant \( C \), we can write:

\[ p_{n} = \frac{p_{n}}{\sum_{j=0}^{N} p_{j}} \] (6)

\( p_{j} \) may be written as follows:

\[ p_{j} = C \times Q'(T,V-v_{s},N-j,v_{s},j) \]

(7)

By invoking the chemical potential definition we obtain:

\[ Q(T,V-v_{s},N-j) = Q(T,V-v_{s},N) \exp \left( \frac{\mu}{k_{B}T} \right) \]

(8)

By defining

\[ A_{N-j}^{s} = -k_{B}T \ln Q'(T,V-v_{s},N-j,v_{s},j) \]

(9)

\[ A_{j}^{s} = -k_{B}T \ln Q(T,V,v_{s},j) \]

(10)

\[ A_{N-j}^{b} = -k_{B}T \ln Q(T,V-v_{s},N-j) \]

(11)

\[ A_{j}^{b} = A_{N-j}^{b} - A_{N-j}^{s} - A_{j}^{s} \]

(12)

it is obtained

\[ p_{j} = C \times Q(T,V-v_{s},N) \exp \left[ -\frac{(A_{j}^{s} + A_{j}^{b})}{k_{B}T} \right] \lambda^{j} \] (13)

where \( \lambda = e^{\mu/k_{B}T} \). Hence, we have:

\[ p_{n} = \frac{\exp \left[ n_{s} \mu_{g}^{0} - A_{n}^{s} - A_{n}^{b} \right]}{1 + \sum_{j=1}^{n_{s}} \exp \left[ j \mu_{g}^{0} - A_{j}^{s} - A_{j}^{b} \right] \lambda^{j}} \] (14)
where $\mu_0^G$ is the gas-phase chemical potential at the reference pressure $P^0$, and $a$ is the activity:

$$a = \frac{f}{P^0}$$

The term $A_j^q$ may be regarded as a free energy of interaction between the subsystem and the bath [17]. If we assume that the bath and the subsystem weakly interact, then $A_j^q$ is small. Now, we define:

$$K_j(T) = \exp \left[ \frac{j\mu_0^G - A_j^S}{k_BT} \right]$$  \hspace{1cm} (15)

If the system may be divided into identical weakly-interacting [34] subsystems then we can state that $\Xi = \xi^M$ where [22]:

$$\xi = 1 + \sum_{j=1}^{n_s} K_j a^j$$  \hspace{1cm} (16)

Here, $\xi$ is the subsystem’s grand canonical partition function and $\Xi$ is the grand canonical partition function. We can calculate the saturation ($q$) as follows:

$$q = \frac{n}{n_s} \sum_{j=1}^{n_s} \frac{jK_j a^j}{1 + \sum_{j=1}^{n_s} K_j a^j}$$  \hspace{1cm} (17)

The term $K_j$ can be considered as an adsorption equilibrium constant. Therefore, by similarity with chemical equilibrium constants, we can propose the following relation:

$$\ln K_j = \ln K_j^q - \frac{\Delta h_j}{RT}$$  \hspace{1cm} (18)

where $\ln K_j^q$ and $\Delta h_j$ are a change of entropy and enthalpy, respectively, related with the adsorption of $j$ molecules on a representative microscopic subsystem at the reference pressure $P^0$. Eq. (17) was proposed by Langmuir [35] for the case in which a site can hold several molecules and the adsorbent is a set of non-interacting sites. In light of his proposal, the term $K_j$ is partitioned as follows:

$$K_j = \frac{1}{j!} \prod_{i=1}^{j} R_i$$  \hspace{1cm} (19)

In a similar fashion, $R_j$ behaves as $K_j$:

$$R_j = R_j^q \exp \left( -\frac{\Delta h_j}{RT} \right)$$  \hspace{1cm} (20)

where

$$R_j^q = \frac{jK_j^q}{K_j^{q-1}}$$  \hspace{1cm} (21)

$$\Delta h_j = \Delta h_{j-1} - \Delta h_{j-1}$$  \hspace{1cm} (22)

Thus, in order to fit an individual isotherm using Eq. (17), the adjustable parameters are $\{R_j\}$ instead of $\{K_j\}$. For the case in which several isotherms at different temperatures have been measured, the adjustable parameters are $\{\ln R_j\}, \{\Delta \eta_j\}$, and $q_m$, a total of $2n_s + 1$ parameters.

The present model suggests that $\xi \rightarrow \Xi$ as the subsystem volume is increased. Thus, in order to predict $q$, we should assume that the maximum number of molecules $n_s$ is large enough such that $A_j^q \rightarrow 0$ for all $j$ [17]. However, if we assume that each $R_j$ is an adjustable parameter, this would give us a high number of adjustable parameters with poor statistical confidence [31]. A solution for this problem could be assume $n_s$ as a small number of molecules that adsorb on a microscopic imaginary subsystem and the parameters $\{R_j\}$ as representative parameters of the experimental adsorption isotherm. Thus, we are assuming that the adsorbate system can be divided into an abstract and idealized grand ensemble of subsystems. The characteristics of the adsorbate+adsorbent system like molecule-surface and molecule-molecule interactions are included abstractly in these subsystems. This is an ad hoc guess because we are not claiming that this idealized system exists, but this assumption is a convenient picture that allows us to apply the cell model even to heterogeneous systems despite this model was originally conceived to study relatively homogeneous systems like zeolites.

Accordingly with Eq. (6), the probability that a subsystem with $n$ adsorbed molecules will be found is (assuming ideal gas phase):

$$p_n = \frac{K_n (P/P^0)^n}{\xi}$$  \hspace{1cm} (23)

Eq. (17) can be written as:

$$\theta = \frac{1}{n_s} \sum_{j=1}^{n_s} \frac{jP_j}{1 + \sum_{j=1}^{n_s} R_j a^j}$$  \hspace{1cm} (24)

Here, $\theta = q/q_m$, and $f_j$ is a fraction of molecules that can be found in subsystems with $j$ molecules. It is known that, at low pressures, the leading term in Eq. (24) is $f_1$ (as stated by the Henry’s law), and, as the pressure increases, the leading term is $f_2$. Similarly, in a certain pressure range, each $f_j$ term significantly contributes to the fractional coverage. Therefore, each parameter $K_j$ is estimated with data taken in a certain range of the saturation $q$. Hence, for intervals where there is not enough data, these parameters will give large uncertainties.

The general isotherm (Eq. (17)) and its simplifications have been useful to fit sets of isotherms of adsorption of gases and vapors on zeolite adsorbents at different temperatures, where the experimental isotherms show clearly a saturation limit, or are reported within the same range of saturation [24, 25, 26, 27, 28, 29, 30]. However, a great number of adsorption systems do not show this behavior because experiments typically are performed within the same pressure range; therefore, the isotherms apparently show that the saturation limit depends on temperature (i.e., $q_m$ tend to increase with a decrease in temperature). Now, consider a certain isotherm at
temperature $T_1$, if we consider that $n_s = 3$, we have the following adjustable parameters: $K_1$, $K_2$, $K_3$, and $q_m(T_1)$. On the other hand, suppose that we have a second isotherm at temperature $T_2$ and its apparent saturation limit is $q_m(T_2)$; if $T_2 < T_1$, then $q_m(T_2) > q_m(T_1)$. This would suggest that, as the temperature decreases, new subsystems are created, but this would be a physical inconsistency. To solve this problem, we introduce a new equilibrium parameter $K_{n+1}$ that take into account the adsorption of an extra molecule on a subsystem at high pressures and low temperatures. Because this new parameter describes the adsorption at these conditions, it is possible that there is not enough experimental data to estimate $\ln R_n^{(n+1)}$ and $\Delta h^{(n+1)}$, then it is plausible to assume that $R_{n+1} = R_n$ and write
\begin{equation}
K_{n+1} = \frac{R_n}{n_s + 1} K_n
\end{equation}
Thus, we are assuming that the change of both entropy and enthalpy of adsorption of the $(n_s + 1)$th molecule on a microscopic cell is the same for the adsorption of the $n$th molecule (i.e., $R \ln R_{n+1}^{(n+1)} = R \ln R_n^{(n+1)}$ and $\Delta h_{n+1} = \Delta h_n$). This result is generalized as follows:
\begin{equation}
K_{n+1} = \frac{R_n^{(n+1)}}{n_s + 1} K_{n-1}
\end{equation}
Now, $\xi$ becomes:
\begin{equation}
\xi = 1 + \sum_{j=1}^{n_s} K_j a^j
\end{equation}
and the isotherm is:
\begin{equation}
q = \frac{q_m}{n_s + 1} \sum_{j=1}^{n_s} K_j a^j
\end{equation}

### 2.2 A Simplified Adsorption Isotherm

In order to reduce the number of adjustable parameters and reduce confidence intervals around parameters estimates, let us re-express Eq. (17) as follows (assuming ideal gas phase):
\begin{equation}
q = \frac{q_m}{n_s + 1} \sum_{j=1}^{n_s} \frac{Z(T, \nu_n, j)}{(j - 1)!(k_B T/P_0)} a^j
\end{equation}
here $a = P/P_0$. It can be shown that:
\begin{equation}
k_B T^2 \frac{d}{dT} \ln \left[ \frac{Z(T, \nu_n, j)}{(k_B T/P_0)} \right] = \langle \mathcal{U}_S(j) \rangle - j k_B T
\end{equation}
where
\begin{equation}
\langle \mathcal{U}_S(j) \rangle = \frac{1}{Z(T, \nu_n, n)} \int dR \mathcal{U}_S(R) \exp \left[ - \frac{\mathcal{U}_S(R)}{k_B T} \right]
\end{equation}
because the adsorption energy $\langle \mathcal{U}_S(j) \rangle$ is usually greater than $j k_B T$, then we can assume that the latter term is a constant $j k_B T$, where $T$ is a mean temperature. Integration of Eq. (29) gives:
\begin{equation}
\ln \left[ \frac{Z(T, \nu_n, j)}{(k_B T/P_0)} \right] = K_j \exp \left[ - \frac{\langle \mathcal{U}_S(j) \rangle - j k_B T}{k_B T} \right]
\end{equation}
As an special case, let us assume that the potential energy $\langle \mathcal{U}_S(j) \rangle$ can be written as follows:
\begin{equation}
\langle \mathcal{U}_S(j) \rangle = \sum_{n=1}^{j} \mathcal{U}_{F-M}(R_n) + \sum_{n=m}^{j} \mathcal{U}_{M-M}(R_n, R_m)
\end{equation}
where $\mathcal{U}_{F-M}$ and $\mathcal{U}_{M-M}$ are the field-molecule and the molecule-molecule interaction potentials, respectively. Now, we obtain:
\begin{equation}
\langle \mathcal{U}_S(j) \rangle = j! \mathcal{U}_{F-M} + \frac{j(j-1)}{2} \mathcal{U}_{M-M}
\end{equation}
For the sake of simplicity let us assume that the potential energy $\langle \mathcal{U}_S(j) \rangle$ do not depend on $j$ and there is a temperature $T^*$ such that $K_j = (K^o)^j$, where $K^o$ is the pre-exponential term in the Henry’s constant. Under these assumptions, it is obtained the adsorption isotherm:
\begin{equation}
q = \frac{q_m}{n_s + 1} \sum_{j=1}^{n_s} \frac{e^{-(E_{M-M}/RT)}}{j!} (K^o a)^j
\end{equation}
where
\begin{equation}
E_{M-F} = -N_A \langle \mathcal{U}_{F-M} \rangle
\end{equation}
\begin{equation}
E_{M-M} = -N_A \langle \mathcal{U}_{M-M} \rangle
\end{equation}
here, $N_A$ is the Avogadro’s constant. If $\langle \mathcal{U}_{F-M} \rangle$ and $\langle \mathcal{U}_{M-M} \rangle$ depend on $j$, we can introduce the equation:
\begin{equation}
q = \frac{q_m}{n_s + 1} \sum_{j=1}^{n_s} \frac{e^{-\Delta h_j/RT}}{j!} (K^o a)^j
\end{equation}
comparing with Eq. (27) we have:
\begin{equation}
K_j = \frac{(K^o)^j}{j!} e^{-\Delta h_j/RT}
\end{equation}
For this simplified isotherm, from Eq. (26), we have:
\begin{equation}
K_{n+1} = \frac{K^o e^{-(\Delta h_{n+s} - \Delta h_{n+s-1})/RT}}{n_s + 1} K_{n+1}
\end{equation}
Here, the fitting parameters are $\{\Delta h_j\}$, $K^o$, and $q_m$, a total of $n_s + 2$ adjustable parameters. We can connect this result with
the empirical isotherm proposed by Ruthven [32] \((l = 0)\):\[ q = \frac{\sum_{j=1}^{n} A_j (KP)^j}{1 + \sum_{j=1}^{n} A_j (KP)^j} \quad A_1 = 1 \] (40)
in this Eq., \(K\) is the Henry’s constant, and \(A_j\) is an empirical parameter. The parameter \(A_j\) is expressed as follows:\[ A_j = \exp \left( -\frac{\Delta h_j}{k_b T} \right) \] (41)and\[ K = \frac{K^0}{p_0} \] (42)thus, the Henry’s constant in Ruthven’s Eq. is replaced by the pre-exponential term \(K^0/p_0\).

If the term \(k_b T\) is not precise, Eq. (37) can be written as\[ q = \frac{q_m}{n_s + l} \frac{\sum_{j=1}^{n_s+l} e^{-\Delta u_j/RT} (K^0 a^j)^j}{1 + \sum_{j=1}^{n_s+l} e^{-\Delta u_j/RT} (K^0 a^j)^j} \] (43)where\[ T' = \frac{T}{T^0} \] (44)\[ \Delta u_j = N_A \langle \delta q_j \rangle \] (45)here, \(T^0\) is a reference temperature (e.g., 1 K).

### 2.3 Isothermic Heat of Adsorption

From Eq. (15) we have\[ \Delta h_j = u_j - jh_j^0 \] (46)where \(u_j\) and \(h_j^0\) are the energy of \(j\) molecules in a subsystem and the molar enthalpy of the gas phase at \(P^0\), respectively, \(\Delta h_j\) is the change of enthalpy related to the adsorption of \(j\) molecules on a subsystem. It can be noticed that, in principle, \(\Delta h_j\) is temperature-dependent, but for the sake of simplicity, we have assumed that both \(h_j^0\) and \(u_j\) are temperature-independent. The isothermic heat of adsorption can be calculated by means of the following formula [36]:\[ q^{st} = h_j^0 - u_s \] (47)where \(h_j^0\) and \(u_s\) are the molar enthalpy of the gas phase and adsorbate molar internal energy respectively. For any function \(g_j\), define:\[ \langle g_j \rangle_0 = \sum_j P_j g_j \]

It is easy to show that [37, 38]\[ -q^{st} = \frac{\langle j\Delta h_j \rangle_0 - n_s \theta \langle \Delta h_j \rangle_0}{\langle \theta^2 \rangle_0 - n_s^2 \theta^2} \] (48)

where \(\theta = q/q_m\). From the above eq. the two following limits arise:

\[
\begin{align*}
\lim_{\theta \to 0} q^{st} &= -\Delta \theta_1 \\
\lim_{\theta \to 1} q^{st} &= -\Delta \theta_{\text{ns}}
\end{align*}
\] (49) (50)

Equivalently, if Eq. (43) is used, the differential heat of adsorption can be calculated as follows:

\[ -q^d = \frac{\langle j\Delta u_j \rangle_0 - n_s \theta \langle \Delta u_j \rangle_0}{\langle \theta^2 \rangle_0 - n_s^2 \theta^2} \] (51)

For the experimental isotherms studied here, both simplified isotherms (Eqs. (37) and (27)) to several experimental adsorption data are shown in Tables 1 and 2; the parameters are tabulated with their corresponding marginal confidence intervals [39, 40]. The study of these confidence intervals is necessary to avoid over-interpretation of the parameters [41] and to estimate uncertainties in predicted thermodynamic properties. The parameter \(ln K^0\) (or \(ln K^0\)) was used instead of \(K^0\) (or \(K^0\)) due to the restriction \(K^0 > 0\) (for all \(j\)). To analyze the fittings precision, the following deviation percentage parameter was used:

\[ D = \frac{100\%}{N_T} \times \sum_{j=1}^{N_{temp}} \sum_{i=1}^{N_T} \left| \frac{q(P_i, T_j) - q_{\exp}(P_i, T_j)}{q_{\exp}(P_i, T_j)} \right| \] (52)

where \(N_{temp}\) is the number of isotherms, \(N_T(j)\) is the number of experimental data taken at \(T_j\) temperature, \(N_T\) is the total number of experimental data, \(q(P_i, T_j)\) is the calculated saturation, and \(q_{\exp}(P_i, T_j)\) is the experimentally measured saturation. It can be noticed in Table 1 that the deviation parameter \(D\) in all cases is less than 5%.

In Fig. 1 the fitted and experimental isotherms of SF\(_6\) adsorption on pillared clay (designated as W-A(673) [42]) are shown\(^1\), it was used Eq. (37). It can be noticed a good agreement between the experimental data and Eq. (37). For this set of isotherms, the correction term (Eq. (39)) was used \((l = 1)\) and it was obtained a deviation of 2.97%. If this correction is not applied \((l = 0)\) the deviation is 5.2%. Therefore, in

\(^1\)For this system, the saturation is expressed as a volume at 101.325 kPa and 273.15 K
Table 1: Estimated parameters for several systems using Eq. 37 $^{a,b,c,d}$

| System                        | $q_m$ (or $v$) mmol g$^{-1}$ (or cm$^3$ g$^{-1}$) | $\ln K^a$ | $-10^{-3} \times \Delta h_j/R$ | D (°) | Temperature range (K) | Pressure range (kPa) |
|-------------------------------|--------------------------------------------------|-------------|---------------------------------|-------|------------------------|-----------------------|
| SF$_6$+W-A(673)$^{[42]}$ $l = 1$ | 23.89 ± 0.44                                     | -13.67 ± 0.16 | 3.107 ± 0.055                   | 2.97  | 266.5-297.5            | 0.1-100               |
| C$_3$H$_8$+W-A$^{[42]}$ $l = 1$ | 34.6 ± 3.9                                       | -14.65 ± 0.30 | 3.391 ± 0.096                   | 3.2   | 267-298                | 0.1-100               |
| HFC-227ea+AC$^{[43]}$ $l = 0$  | 3.87 ± 0.27                                      | -16.67 ± 0.27 | 6.066 ± 0.098                   | 2.36  | 283.15-363.15          | 0.01-100              |
| HFP+AC$^{[43]}$ $l = 0$       | 3.87 ± 0.20                                      | -15.66 ± 0.20 | 5.429 ± 0.075                   | 2.53  | 283.15-363.15          | 0.01-100              |
| CO$_2$+ZC$^{[44]}$ $l = 1$    | 4.82 ± 0.39                                      | -15.71 ± 0.29 | 5.03 ± 0.10                     | 3.84  | 273.15-353.15          | 0.05-100              |
| CO$_2$+SG$^{[45]}$ $l = 4$    | 14.5 ± 1.0                                       | -15.22 ± 0.10 | 3.068 ± 0.030                   | 1.47  | 278-328                | 50-3400               |

$^a$ In all cases, $P^0$ is expressed in kPa.
$^b$ Abbreviations: activated carbon (AC), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227a), hexafluoropropene (HFP), zeocarbon (ZC), silica gel (SG).
$^c$ The parameters $\Delta h_j$ are tabulated in increasing order of $j$, e.g., for the SF$_6$+W-A(673) system, $\Delta h_1/R = -3.107 \times 10^3$, $\Delta h_2/R = -6.112 \times 10^3$, and so on.
$^d$ For SF$_6$+W-A(673) and C$_3$H$_8$+W-A systems, the saturation is expressed in cm$^3$ g$^{-1}$ at 101.325 kPa and 273.15 K, and for the remaining systems it is expressed in mmol g$^{-1}$.

Table 2: Estimated parameters for the adsorption data presented by Watson et al. $^{[46]}$ using Eq. 27 (l=0)$^{a,b,c}$

| System | $q_m$ mmol g$^{-1}$ | $\ln R_j^c$ | $-10^{-3} \times \Delta h_j/R$ | $\Delta (\overline{h})_j/R$ | D (°) | Temperature range (K) | Pressure range (kPa) |
|--------|---------------------|-------------|---------------------------------|-----------------------------|-------|------------------------|-----------------------|
| CH$_4$+MSC | 4.412 ± 0.067       | -14.4 ± 1.5 | 2.81 ± 0.41                     | 2.29                        | 148-298 | 1-4000                |
| CO$_2$+MSC | 5.87 ± 0.14         | -13.7 ± 1.3 | 3.26 ± 0.40                     | 1.41                        | 223-323 | 25-5200               |
| N$_2$+MSC | 5.75 ± 0.12         | -15.6 ± 1.1 | 2.71 ± 0.31                     | 3.14                        | 115-298 | 0.01-5000             |

$^a$ In all cases, $P^0$ is expressed in kPa.
$^b$ Abbreviation: molecular sieving carbon (MSC).
$^c$ As in 1, the parameters $\ln R_j^c$ and $\Delta (\overline{h})_j/R$ are tabulated in increasing order of $j$, for example, for the CH$_4$+MSC system, $\ln R_1^c = -14.4$, $\ln R_2 = -13.88$, $\Delta (\overline{h})_1/R = -2.81 \times 10^3$, $\Delta (\overline{h})_2/R = -1.92 \times 10^3$. 

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this case, the correction term gives a better result. Fig. 1 suggests that Eq. (37) is useful for isotherms with complex shapes like those reported in Ref. [42]. The experimental isotherms shown in Fig. 1 were also fitted using the 5-parameter Toth isotherm and it was obtained a deviation of 17.8%; a value that is greater than that obtained with Eq. (37). On the other hand, Eq. (27) could be also used to fit these experimental isotherms, but more parameters would be necessary and this would lead to large error bars and thermodynamic properties with large uncertainties. Bandosz et al. [42] reported additional single-component experimental isotherms of propane and sulfur hexafluoride adsorption on various heat-treated pillared clays; a total of six adsorbate+adsorbent systems were studied. Given that the results are similar, here only two analyzed systems are reported in Table 1. But, for each of the six adsorbate+adsorbent systems the deviation was within 1 and 3%.

Fig. 2 shows the estimated isosteric heat of adsorption as a function of adsorbed volume and the corresponding marginal confidence intervals [39, 40] for the SF₆+W-A(673) system. This Fig. shows that the isosteric heat of adsorption is nearly constant around 25.5 kJ/mol. Bandosz et al. [42] used a virial type isotherm [47, 48] and the adsorption isosteric heat vs adsorbed volume plot obtained by them presents some oscillations near zero saturation around 25 kJ/mol; this result does not agree with that obtained here by means of Eq. (48). These differences could be due to the method used by Bandosz et al. [42], they fitted small subsets of 15 adsorption data by using the virial type isotherm and used four parameters to fit each subset. Although this method is appropriate, the error bars reported by them correspond to standard deviations in calculated isosteric heats of adsorption. If 95% marginal confidence intervals are used, the error bars at low coverage would be even larger than those reported by them and the isosteric heats reported here would fall within such uncertainty region.

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To illustrate the dependence of the isosteric heat of adsorption in terms of temperature, plots of $q^s$ vs $T$ at three different saturations are shown in Fig. 3. As expected, the isosteric heat of adsorption does not significantly change within the experimental range of temperatures. This is a typical behavior of the isosteric heat of adsorption that is observed in both experiments and molecular simulations. In the case in which it is necessary to take into account the dependency of isosteric heat of adsorption on temperature, the well known thermochemical formula [49] to calculate chemical equilibrium constants could be used to estimate $\ln K_j$ as a function of temperature in Eq. (15); an empirical model for the heat capacity would be necessary.

The fitting of the experimental isotherms of adsorption of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) on activated carbon is shown in Fig. 4. As in the previous case, there is a good agreement between model and experiment; the correction term
was not necessary \((l = 0)\). Due to the complex pore structure of activated carbon, it is difficult to consider a subsystem as any specific region of the real adsorbent, for this reason it is convenient to regard each cell as a representative subsystem. The isosteric heat of adsorption calculated by using Eq. \((48)\) and Toth equation are shown in Fig. 5. It can be noticed that both curves fairly agree. The differences are attributed to the fact that Yun et al. [43] only used two isotherms to calculate the isosteric heat of adsorption; they employed the parameters of each isotherm and the Clausius-Clapeyron equation to obtain the \(q^\alpha\) vs \(q\) plot, in contrast, here the complete set of experimental isotherms was used. A problem with the method used by Yun et al. [43] is that the isosteric heat of adsorption is influenced by uncertainties in adsorption data, and hence, very reliable isotherms are necessary to determine \(q^\alpha\).

In Fig. 6, it is shown the adsorption isotherms of CO\(_2\) on zeocarbon [44] and the fractions of molecules distributed among cells at 273.15 K and 313.15 K. The zeocarbon synthesized by Lee et al. [44] is a zeolite X/activated carbon mixture composed by 38.5 mass % zeolite X, 35 mass % activated carbon, 10 mass % inert silica, and 16.5 mass % zeolite A and P. For this system, Eq. \((37)\) accurately fits the experimental data \((D = 3.8\%)\), and the correction term \((l = 1)\) in this case reduces the deviation by 2 % with respect to \(l = 0\). The deviation is less than that obtained by using the Toth equation, which is one of the most used equations to fit these kind of adsorption data. Given that the zeocarbon is a zeolite/activated carbon composite, from these results, it can be inferred that the method used here is empirical. Consequently, the assumption that the adsorbate phase may be divided into identical weakly-interacting subsystems and the fictitious representative grand ensemble of subsystems are just convenient pictures for fitting and correlation purposes.

As it was mentioned, at low pressures the leading term is \(f_1\) and each \(f_j\) significantly contributes in a certain region of the isotherm. It can be noticed in Fig. 6a that near 100 kPa, the saturation \((q)\) changes in approximately 0.5 mol kg\(^{-1}\). Accordingly with the fitting method used here, at the lowest experimental temperature, for which at high pressures the saturation is approximately \(q_m\), the leading term is \(f_{k+1}\), as shown in Fig. 6b. However, as temperature increases in the high experimental pressure region, the isotherm is a combination of several fractions \(f_j\). For example, Fig. 6b shows that the isotherm at 313.15 K in the high pressure region is a combination of \(f_5, f_4\) and \(f_3\). When temperature is further increased, the term \(f_5\) does not contribute to the isotherm. If the correction term is not used and \(n_s = 4\), the plot of \(f_4\) vs \(P\) is quite similar to that shown in Fig. 6c for \(f_5\) and thus, this term \((f_4)\) does not significantly contribute to the isotherm at 313.15 K. For this reason, it was necessary to propose the correction terms shown in Eqs. \((26)\) and \((39)\), these Eqs. assure that high-order fractions depend on parameters that substantially contribute to estimate each isotherm within the experimental temperature range. Because of the specific characteristics of each adsorbate/adsorbent system, it is difficult to establish a priori whether the correction term is necessary, it must be tested whether this correction reduces the fitting standard deviation.

In Table 2, the results of the fittings of data reported in Ref. [46] are presented. In this case, Eq. \((27)\) was used without any correction. For the CO\(_2\)+MSC and N\(_2\)+MSC systems, Eq. \((27)\) gives better results (in terms of deviation) than the simplified model (Eq. \((37)\)). With Eq. \((37)\) the deviation is around 3.5% \((l = 0)\), whereas Eq. \((17)\) gives deviations less than 3 %. Also, the deviation obtained using Eq. \((27)\) is less than that obtained by using the Toth equation; this is also confirmed by F-tests. The confidence intervals for \(\ln R_p^c\) are larger than those obtained for \(\ln K^c\) in Table 1, this could be caused by parameter correlation effects. To fit this set of isotherms, Watson et al. [46] used the Toth isotherm and also obtained large confidence

![Figure 4: Comparison between the experimental data of HFC-227ea adsorption on activated carbon [43] and Eq. (37); symbols: experiment, solid line: Eq. (37).](image)

![Figure 5: Isosteric heat of HFC-227ea adsorption on activated carbon calculated; dotted/dashed line: calculated by Yun et al. [43], solid line: Eq. (48), dotted lines: 95% marginal confidence intervals for Eq. (48).](image)
The advantage of the present models is the flexibility of setting the number of adjustable parameters; this condition is essential to fit isotherms with complex shapes. It is known that some of the most widely used empirical isotherms to describe type I isotherms are Sips, Toth, and Dubinin type \([50, 51, 52]\) isotherms. These Eqs. do not reduce to the correct Henry’s law limit; except the Toth isotherm, but this overestimates the Henry’s constant \([53]\). In contrast, the isotherm models studied here have the advantage that they present the correct Henry’s law limit and thus they can be used to estimate this constant\(^2\). Despite its advantages, the model studied here cannot give site energy and pore size distribution. However, although the model does not explicitly take into account the adsorbent heterogeneity, the number of parameters and the degree of the polynomial \(\xi\), which are related to the subsystem size, give an idea of the variety of adsorbent sites and molecule-molecule interactions because the system size is related to these characteristics of the adsorbate+adsorbent system.

### 4 Conclusions

The cell model of adsorption was reviewed and analyzed by using the SSGE method and a simplified accurate isotherm model is proposed (Eq. (37)). It was found that the Eqs. (27) and (37) can be applied to fit experimental data of adsorption of gases and vapors on microporous heterogeneous adsorbents; these isotherms give relatively accurate fittings. A simple correction that improve the fitting results is proposed. However, in some cases this correction may not be necessary, must be tested. Additionally, for systems in which the experimental temperature range is large, it is suggested that the dependence of \(\Delta h_j\) on temperature must be considered and a model for both gas and adsorbate phase heat capacity could be required. Finally, the model based on an idealized and abstract grand ensemble of subsystems presented here is useful to correlate single-component adsorption data and the corresponding thermodynamic properties of interest. Specifically, the model is useful to fit type I isotherms, i.e., the reversible micropore filling region of the experimental adsorption isotherm. The advantages of the present model are the correlation accuracy of both adsorption and thermodynamic data, the flexibility to set the number of adjustable parameters and to consider variations of \(\ln K_j\) with temperature, and the possibility of regarding adsorptive as a real gas phase. However, the method studied here does not consider explicitly the pore size and adsorption energy distribution, but the size of a representative subsystem gives an idea of the adsorbent heterogeneity because the size of the subsystem depends on this factor.

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