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Kinetic Derivation of Common Isotherm Equations for Surface and Micropore Adsorption

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Abstract

The Langmuir equation is one of the most successful adsorption isotherm equations, being widely used to fit Type I adsorption isotherms. In this article we show that the kinetic approach originally used by Langmuir for 2D monolayer surface adsorption can also be used to derive a 1D analogue of the equation, applicable in ultramicropores with single-file diffusion systems. It is hoped that such a demonstration helps dispel the idea that the

Langmuir isotherm equation cannot apply to some micropores as more than a mathematical correlation. We furthermore seek to extend the intuitive insight provided by the simple kinetic derivation of the Langmuir equation to other isotherm equations capable of modelling Type I isotherms. The kinetic approach is thus also used to derive the Volmer, Fowler-Guggenheim and Hill-de Boer equations, both for surface (2D adsorbed phase) and micropore adsorption (1D and 3D adsorbed phases). It is hoped that this will help make it more intuitively clear that these equations can be used as phenomenological models in some instances of adsorption in micropores.

Keywords

Micropores; Langmuir isotherm; Volmer isotherm; Localised adsorption; Distributed adsorption

Introduction

Langmuir pioneered the kinetic approach to the derivation of adsorption isotherms in 1918 [1], by deriving an expression that considers adsorption of gas-phase molecules on specific sites of the surface, upon hitting on it at a rate given by the Kinetic Gas Theory. This approach had scant sequence, being used only in the derivation of the BET and GAB equations [2]. The more powerful and simple thermodynamic (classic and statistical) approaches proved much more attractive and productive. In porous solids, even the kinetics of adsorption could not be appropriately described using the kinetic approach of Langmuir, since diffusion through the pores is typically the rate-controlling mechanism.

With the discovery of the distributed nature of London forces and the development of the concept of adsorption potential, it was realised that purely localised adsorption very

seldom exists for physical sorption [3]. Nonetheless, the elegance, simplicity and ability to produce fitting parameters with clear physical meaning made the Langmuir equation one of the most widely used adsorption isotherm equations. So much so that Type I adsorption isotherms are often called “Langmuir-like”, or simply “Langmuir” [4-6]. We therefore believe that other adsorption isotherm equations would greatly benefit from the insight gained from a kinetic derivation.

The simplest thermodynamic approach to adsorption is expressed by the Gibbs adsorption isotherm. In another article [7] we proposed that the Gibbs adsorption isotherm, and the equations derived from it, can be accurately applied to some micropores, besides surfaces, by considering one- (1D) and three-dimensional (3D) adsorbed phases. 1D systems represent ultramicropores with single-file diffusion, while 3D systems represent large ultramicropores and small supermicropores where merging of adsorption potentials from opposite walls creates an adsorption potential that is radially uniform [8]. The simplest equations derived from the Gibbs adsorption isotherm are represented in Table 1. These five equations represent the most basic types of adsorption; localised or distributed, with or without lateral interactions. All can generate Type I isotherms, and the Hill-de Boer and Fowler-Guggenheim equations can also generate Type V isotherms. For 3D adsorbed phases, the concept of localised adsorption does not apply, and, thus, the Langmuir and Fowler-Guggenheim equations are only considered for localised 1D and 2D adsorbed phases.

Table 1. Different adsorption isotherm equations obtained from the Gibbs equation, for gases, and Type of Adsorption it models. Type of Adsorption can be localised or distributed and with lateral interactions or without lateral interactions. For adsorption of solutes from liquid solutions, pressure is replaced by concentration. The variables in the equations are defined in the text.

Name of Isotherm	Isotherm Equation	Type of Adsorption
Henry	$bP = \theta$	Any
Langmuir [1]	$bP = \frac{\theta}{1 - \theta}$	Localised, without lateral interactions
Fowler-Guggenheim [9]	$bP = \frac{\theta}{1 - \theta} \exp(-c \theta)$	Localised, with lateral interactions
Volmer [10]	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right)$	Distributed, without lateral interactions
Hill-de Boer [11-13]	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \exp(-c \theta)$	Distributed, with lateral interactions

The kinetic derivation of the five isotherm equations of Table 1 will be given below, for 1D, 2D and 3D systems. We hope that by exemplifying a kinetic derivation of the Langmuir equations for 1D systems we may help dispel the idea that it can never represent a physical model of micropore adsorption. To perform these derivations, kinetic arguments as those of Langmuir [1] and de Boer [14, 15] will be used. It will be assumed that adsorbed molecules are hard spheres, behaving according to Newtonian kinematics, and that impacting molecules only interact with the solid upon hitting the surface (2D) or entering the pore (1D and 3D). It should be noted that these crude simplifications are already implicit in the thermodynamic derivations [7]. They will prove to be very powerful in promoting insight into some of the physical realities behind the isotherm equations under consideration, in the same way it occurred with the Langmuir equation.

We should emphasise that we are not proposing that adsorption occurs necessarily or exactly according to the mechanisms proposed in the models. This is especially the case in micropores, where adsorption around the pore mouth plays a decisive role in promoting in-pore adsorption. We seek only to show that simple models such as that originally used

by Langmuir can be used to derive other simple isotherm equations, and that they can be used as easily in micropore adsorption as in monolayer surface adsorption.

Adsorption on a Planar Surface – 2D

Localised Adsorption – The classic Langmuir model

The classic Langmuir model describes adsorption on a surface with discrete adsorption sites. It has been described many times before [14, 16], but a small recapitulation will be very helpful in setting the conceptual framework used for the derivations that follow.

The rate of adsorption is equal to the rate of impact of gas-phase molecules on unoccupied adsorption sites. The rate of impact on a surface is given by the Kinetic Gas Theory, having SI units of $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. If the units desired for the adsorption rate are $\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$, the rate of impact must be multiplied by the specific surface area, with SI units $\text{m}^2\cdot\text{kg}^{-1}$. The surface is not entirely covered by adsorption sites and not all impacts on these are successful, so an extra term, α , is included, representing the fraction of successful impacts on the surface. Finally, not all adsorption sites are free, so the rate of adsorption will be proportional to the fraction of those that are. This fraction is given by $(1 - \theta)$, where θ represents the total amount adsorbed relative to the maximum that can be adsorbed (monolayer coverage). Thus, the equation for the rate of adsorption is

$$r_a = \frac{P}{\sqrt{2\pi MRT}} \cdot \alpha \cdot (1 - \theta) \cdot A \quad (1)$$

where r_a represents the rate of adsorption, A represents the specific surface area of the adsorbent, P represents pressure, M represents molar mass, R represents the ideal-gas constant and T represents absolute temperature.

Desorption is an activated phenomenon, the rate of which is proportional to the amount adsorbed. Therefore, the rate of desorption can be expressed as:

$$r_d = k_d \cdot n \quad (2)$$

where r_d represents the rate of desorption (SI units of $\text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$), k_d represents the frequency of desorption (s^{-1}) and n represents the specific amount adsorbed ($\text{mol} \cdot \text{kg}^{-1}$).

The frequency of desorption is given by,

$$k_d = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where E_a is the activation energy of desorption and k_0 is the maximum frequency of desorption, reached at infinite temperature. The activation energy of desorption is basically the heat of adsorption, that is, $E_a = (-\Delta H)_{ads}$.

Equating the rate of adsorption with the rate of desorption, and considering that $\theta = n/n_{max}$, results in the Langmuir equation,

$$r_a = r_d \Leftrightarrow bP = \frac{\theta}{1 - \theta} \quad (4)$$

where b is the so-called affinity constant, and,

$$b = \frac{K_H}{n_{max}} \quad (5)$$

where n_{max} represents the maximum specific amount that can be adsorbed and K_H is Henry's constant, which can be expressed as

$$K_H = \frac{\alpha \cdot A}{k_d \sqrt{2\pi MRT}} \quad (6)$$

Distributed Adsorption – Volmer Equation for Surfaces

The derivation of an equation for distributed monolayer adsorption will now be described, using the same kinetic approach as for localised adsorption. From the thermodynamic derivation [13, 16], we know the Volmer equation is the correct final result. As a starting point, it must be considered, as for the thermodynamic derivation, that adsorption occurs on a uniform adsorption potential on the surface of the adsorbent. This means that, when in the adsorbed phase, the molecules are free to slide through the surface and bump into each other, as a two-dimensional gas [15]. One of the key variables used for the characterisation of the adsorbed phase is the molar area of the system, defined as:

$$a \equiv \frac{A}{n} \quad (7)$$

When a monolayer has been formed, the specific amount adsorbed is at its maximum, n_{max} , and the molar area at its minimum, a_0 . The minimum molar area is approximately the molar area of a single adsorbed molecule, $a_0 = a_{molecule}$.

The desorption rate is modelled in the same manner as for localised (Langmuir) adsorption,

$$r_d = k_d \cdot n \quad (8)$$

where

$$k_d = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right), \quad E_a = (-\Delta H)_{ads} \quad (9)$$

However, the adsorption rate cannot be described by Eq. (1). The fraction of unoccupied surface, $(1 - \theta)$, does not correspond to the surface available for impact of incoming gas molecules, as it occurs for localised adsorption. The freedom of movement leads to the existence of a random distribution of intermolecular distances, unlike the uniform distribution of localised adsorption. An impact is successful, or not, depending on the presence of molecules within the area of impact, as represented in **Figure 1**. This area is exactly the same as the area of an adsorbed molecule, A_0 , or, in molar terms, a_0 . Let us define a variable a_s , the area of the circle centred on the centre of the impact site, and touching the nearest adsorbed molecule, where the s stands for “site”. **Figure 1** shows a_s for a successful impact and an unsuccessful impact. The probability that the available intermolecular area between the adsorbed molecules at the point of impact is large enough for the incoming molecule to hit the surface is therefore $p(a_s > a_0)$. The adsorption rate equation can thus be written as,

$$r_a = \frac{P}{\sqrt{2\pi MRT}} \cdot \alpha \cdot (1 - \theta) \cdot A \cdot p(a_s > a_0) \quad (10)$$

To determine the new probability, it is now only necessary to know the probability distribution function of a_s . This non-negative continuous random variable, $a_s \geq 0$, has a density distribution function, $f(a_s)$, such that,

$$p(a_s > a_0) = 1 - F(a_0) \quad (11)$$

where $F(a_0)$ is the cumulative distribution function of a_s for the molecular area, a_0 .

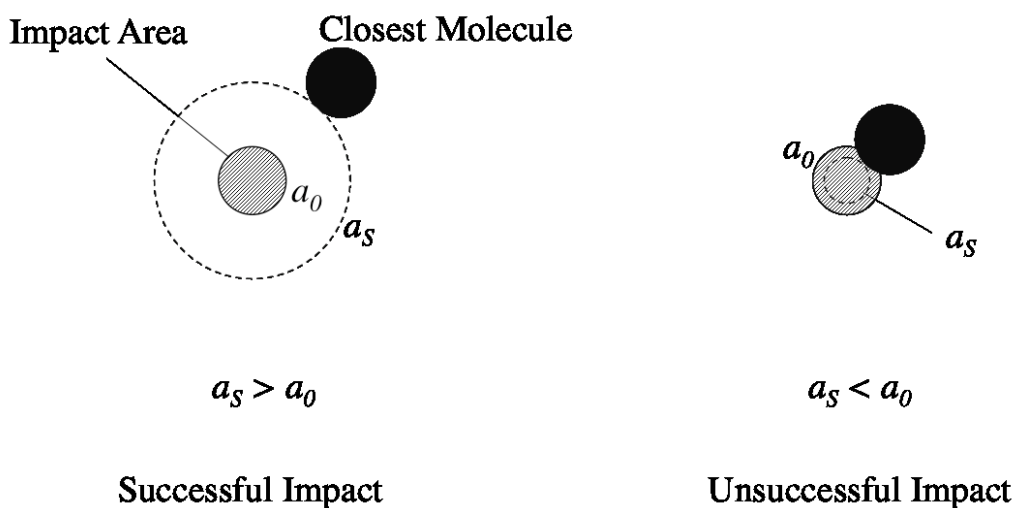


Figure 1. Representation of successful and unsuccessful impacts on the surface, depending on the absence, $a_s > a_0$, or presence, $a_s < a_0$, of an adsorbed molecule on the impact area of the incoming molecule.

It must be considered that, under the model of the two-dimensional gas [15], the adsorbed molecules are randomly distributed on the surface. Therefore, the probability that there is a molecule at a given site is always the same, equal to the fraction of surface area occupied, θ , and independent from the presence of other molecules nearby. The presence of a molecule anywhere on the surface can therefore be seen as a Bernoulli trial, where a given site on the surface either has, or has not, molecules on it, with probability θ . The site area a_s needed to encounter the closest molecule to the impact site (**Figure 1**) can be seen as a first “success” in successive Bernoulli trials. For continuous random variables, the variable counting the number of Bernoulli trials until the first

success has an exponential distribution [17-19]. The corresponding cumulative function of a_s is given by:

$$F(a_0) = 1 - \exp(-\lambda \cdot a_0) \quad (12)$$

where the distribution parameter λ is given by the relationship

$$\lambda = \frac{1}{\langle a_s \rangle} \quad (13)$$

where $\langle a_s \rangle$ is the average of a_s . It is possible to see a_s as the free area at the site of impact, which means its average will be $(a - a_0)$, the total free molar area at the surface. Hence, Eq. (13) can be rewritten as,

$$\lambda = \frac{1}{a - a_0} \quad (14)$$

and, from Eq. (12),

$$F(a_0) = 1 - \exp\left(-\frac{a_0}{a - a_0}\right) \quad (15)$$

Given that,

$$\theta = \frac{a_0}{a} \Rightarrow \frac{a_0}{a - a_0} = \frac{\theta}{1 - \theta} \quad (16)$$

substitution of Eq. (16) into Eq. (15) yields,

$$F(a_0) = 1 - \exp\left(-\frac{\theta}{1 - \theta}\right) \quad (17)$$

Substituting back into the probability equation, Eq. (11), and into the equation for the adsorption rate, Eq. (10), and equating to the desorption rate, Eq. (8), the equation describing the Volmer Isotherm is obtained,

$$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \quad (18)$$

where b is the same as for the Langmuir isotherm, Eqs. (5) and (6).

The Volmer isotherm is significantly less concave than the Langmuir isotherm. This reflects the need for the existence of space between the molecules already adsorbed for new adsorption of gas-phase molecules to take place.

Henry Equation for Surfaces

The Henry isotherm can be obtained directly from the rate equations, Eqs. (1), (2), (8), and (10) by considering that, for low coverage, $(1 - \theta) \approx 1$. That is, the adsorption rate is independent of coverage. The Henry isotherm easily follows from equating the two rates,

$$K_H P = n \quad (19)$$

Applying the $(1 - \theta) \approx 1$ condition directly to the Langmuir and Volmer isotherm equations, the same result is obtained.

1D and 3D Adsorbed phases – Adsorption in Micropores

Application of the kinetic approach to the derivation of adsorption isotherm equations for micropores has one significant difference regarding 2D adsorption; the interface between the two phases is available only to a small fraction of the adsorbate, present at the pore mouths. This influences fundamentally the modelling of both adsorption and

desorption, as the rates of both are now dependent exclusively on concentration at the pore mouths, not the entire adsorbed phase.

It is worth emphasising that, just as for the thermodynamic derivations [7], not all microporous adsorption systems are appropriately represented by the models described below. There are two kinds of micropore adsorption that we propose can sometimes be modelled using the equations in Table 1; ultramicropores with single-file diffusion (1D adsorbed phase) and ultra and supermicropores with a uniform adsorption potential (3D adsorbed phase) adsorbed phases. As mentioned before, only distributed adsorption will be considered for 3D phases.

3D adsorbed phases - Distributed Adsorption

The key variables relevant for describing a 3D system are the specific pore volume of the adsorbent, V (SI units of $\text{m}^3 \cdot \text{kg}^{-1}$), the molar volume of the adsorbent/adsorbate system, $v \equiv V/n$ ($\text{m}^3 \cdot \text{mol}^{-1}$), the average pore mouth area, A_{mouth} ($\text{m}^2 \cdot \text{mouth}^{-1}$), the total specific number of pores, N_{pore} ($\text{pore} \cdot \text{kg}^{-1}$) and the average number of mouths per pore, N_{mouth} ($\text{mouth} \cdot \text{pore}^{-1}$). As with a and a_0 , for v , when $n = n_{max}$, $v = v_0$.

The rate of adsorption on a 3D phase is modelled very similarly to that of a distributed 2D phase, but the area available for adsorption is now only that of the pore mouths. That is,

$$r_a = \frac{P}{\sqrt{2\pi MRT}} \cdot A_{mouth} \cdot N_{pore} \cdot N_{mouth} \cdot p(entry) \quad (20)$$

where $p(entry)$ is the probability of entry of each gas molecule upon hitting the pore mouth. $p(entry)$ is determined by conditions at the interface, the “surface” of the

adsorbed phase inside the pore. In order to model this probability, a new variable is introduced for the 3D system: the interfacial molar area, a_{pore} . A visual representation of the concept of 3D adsorbed phase “surface” can be seen in **Figure 2**.

At equilibrium, the interfacial molar area and pore molar volume are related by

$$\frac{a_0}{a_{pore}} = \frac{v_0}{v} = \theta \quad (21)$$

As for 2D, the fraction of molecules not being deflected at the interface is given by

$$p(\text{entry}) = (1 - \theta) \cdot p(a_s > a_0) \Leftrightarrow p(\text{entry}) = (1 - \theta) \exp\left(-\frac{\theta}{1 - \theta}\right) \quad (22)$$

which can then be substituted into Eq. (20).

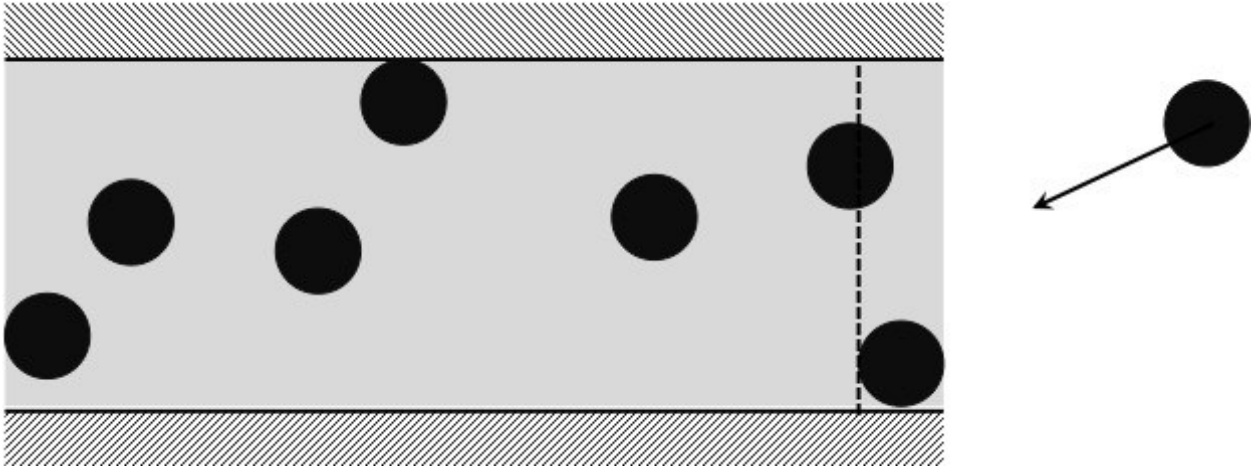


Figure 2. Representation of a 3D adsorbed phase and an incoming gas phase molecule. The dotted line represents the limit of the “surface” of the adsorbed phase, being distanced from the limit of the pore by one molecular diameter. Molecules inside the pore are under the influence of a uniform adsorption potential field.

The desorption rate can also be modelled equivalently to what has been done for 2D. However, in this case, the desorption frequency is not multiplied by the total amount adsorbed, but by the total amount at the interface,

$$r_d = k_d \cdot \frac{1}{a_{pore}} \cdot A_{mouth} \cdot N_{pore} \cdot N_{mouth} \quad (23)$$

Equating r_a and r_d , solving for P and multiplying by a_0 on both sides, the Volmer isotherm equation is obtained,

$$bP = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta}\right) \quad (24)$$

with,

$$b = \frac{K_H}{n_{max}} \quad (25)$$

and,

$$K_H = \frac{a_0 n_{max}}{k_d \sqrt{2\pi MRT}} = \frac{\frac{a_0}{v_0} \cdot V}{k_d \cdot \sqrt{2\pi MRT}} \quad (26)$$

As for 2D, the probability that an incoming molecule is adsorbed in a 3D adsorbed phase (i.e., enters the pore) decreases for increasing θ (Eq. (22)). At high fillings, it is very difficult for molecules to enter the pore, even if it is not completely filled.

Henry Equation for 3D Adsorbed Phases

For 3D adsorbed phases, as for 2D, at low θ , the Volmer isotherm reduces to the Henry equation, Eq. (19). This corresponds to having an adsorption rate that is independent of θ , with so few molecules inside the pores that entry of incoming gas molecules is, effectively, unimpeded. At higher fillings, the limitations to adsorption arising from the

presence of other molecules in the pore become apparent, and Volmer behaviour is established.

1D adsorbed phases

In single-file diffusion systems, when pores are so small that it becomes impossible for molecules to bypass each other (so-called “single-file diffusion” systems), the concept of interfacial “surface” introduced in the previous section no longer applies. This means occupancy limitations to the adsorption rate will depend on the presence of a single adsorbed molecule close to the pore mouth. Such a system is represented in **Figure 3**. If there is an adsorbed molecule within a certain distance of the pore mouth, adsorption will not be possible. Similarly, for desorption, there will not be a molecule always available to desorb close to the pore mouth. The molecule closest to it will, instead, move towards and away from it successively, having a given probability of exiting the pore every time it comes close to the pore mouth.

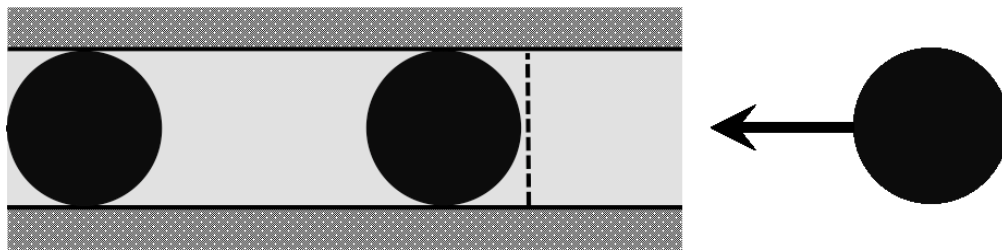


Figure 3. Representation of a single-file diffusion 1D adsorbed phase and an incoming gas molecule. The dotted line represents the minimum distance from the pore mouth to the adsorbed molecule closest to it, d_{ads} , that allows adsorption to take place.

The key new variables used to characterise the system are total specific pore length, L , with SI units of $\text{m}\cdot\text{kg}^{-1}$, and molar length, l , with SI units of $\text{m}\cdot\text{mol}^{-1}$. Similarly to molar area and molar volume, the molar length is defined as:

$$l \equiv \frac{L}{n} \quad (27)$$

Localised Adsorption in 1D Adsorbed Phases

In 1D systems, the concept of localised adsorption is perfectly reasonable. Despite this, the adsorption rate is calculated similarly to that of distributed adsorption in 3D pores,

$$r_a = \frac{P}{\sqrt{2\pi MRT}} \cdot \alpha \cdot A_{mouth} \cdot N_{pore} \cdot N_{mouth} \cdot p(entry) \quad (28)$$

where α represents the fraction of impacts with an angle that allows the molecule to enter the pore.

Since adsorption is localised, $p(entry)$ is the probability that a molecule that has entered the pore adsorbs in a free adsorption site. That is, it is equal to the probability of the adsorption site closest to the pore mouth being free, $1 - \theta$.

The desorption rate also depends on the occupancy of the site closest to pore mouth, but on the probability that the site is occupied. When this happens, a characteristic desorption frequency determines the rate at which molecules leave the mouth of the pore. Therefore, the desorption rate is given by,

$$r_d = k_d \cdot N_{pore} \cdot N_{mouth} \cdot p(site\ is\ occupied) \quad (29)$$

where k_d is given by Eq. (3).

At equilibrium, the probability that the site closest to the pore mouth is occupied is equal to the fraction of occupied adsorption sites, θ . Equating r_a and r_d ,

$$bP = \frac{\theta}{1 - \theta} \quad (30)$$

with,

$$b = \frac{K_H}{n_{max}} \quad (31)$$

and,

$$K_H = \frac{\alpha \cdot A_{mouth} \cdot 1/l_0 \cdot L}{k_d \cdot \sqrt{2\pi MRT}} \quad (32)$$

The kinetic approach thus confirms the result already obtained with the thermodynamic approach [7].

Distributed Adsorption in 1D Adsorbed Phases

For 1D distributed adsorption, the adsorption rate initial formula is exactly the same as for localised adsorption,

$$r_a = \frac{P}{\sqrt{2\pi MRT}} \cdot \alpha \cdot A_{mouth} \cdot N_{pore} \cdot N_{mouth} \cdot p(entry) \quad (33)$$

where α represents the fraction of impacts with an angle that allows the molecule to enter the pore.

In this case, $p(entry)$ is the probability of a molecule existing close enough to the pore mouth so that it prevents an incoming molecule from entering. If the critical distance allowing adsorption is d_{ads} , then,

$$p(entry) = p(d > d_{ads}) \quad (34)$$

where d represents the distance between the pore mouth and the adsorbed molecule closest to it.

Using a similar reasoning as that used with areas for 2D surfaces, it can easily be concluded that the distance between adsorbed molecules is well expressed by an exponential distribution. Assuming that, at equilibrium, the distance to the pore mouth is equivalent to the distance between two adsorbed molecules, it is possible to write,

$$f(d) = \lambda \exp(-\lambda d) \quad (35)$$

$$F(d) = 1 - \exp(-\lambda d) \quad (36)$$

and

$$\lambda = \frac{1}{\langle d \rangle} = \frac{1}{l - l_0} \quad (37)$$

giving

$$f(d) = \frac{1}{l - l_0} \exp\left(-\frac{d}{l - l_0}\right) \quad (38)$$

$$F(d) = 1 - \exp\left(-\frac{d}{l - l_0}\right) \quad (39)$$

where frequency $f(d)$ is given in $\text{mol} \cdot \text{m}^{-1}$ and $F(d)$ is dimensionless. $p(\text{entry})$ can now be expressed in terms of d_{ads} . From Eqs. (34) and (39),

$$p(\text{entry}) = 1 - F(d_{ads}) = \exp\left(-\frac{d_{ads}}{l - l_0}\right) \quad (40)$$

where d_{ads} will be considered to correspond to the length of a single molecule, that is, l_0 .

Therefore,

$$p(\text{entry}) = \exp\left(-\frac{l_0}{l - l_0}\right) = \exp\left(-\frac{\theta}{1 - \theta}\right) \quad (41)$$

The adsorption rate equation can now be rewritten as,

$$r_a = A_{mouth} \cdot N_{pore} \cdot N_{mouth} \cdot \frac{\alpha \cdot P}{\sqrt{2\pi MRT}} \cdot \exp\left(-\frac{\theta}{1-\theta}\right) \quad (42)$$

The desorption rate depends on the frequency with which the molecule closest to the exit “hits” the pore mouth (i.e., is available for adsorption), k_{hit} , and the probability of desorption upon each “hit”, $p(desorb)$. Hence,

$$r_d = N_{pore} \cdot N_{mouth} \cdot k_{hit} \cdot p(desorb) \quad (43)$$

Considering the pore has a smooth and homogeneous internal surface, the “hitting” frequency of adsorbed molecules with the pore mouth is given by

$$k_{hit} = \bar{v} \cdot f(d = 0) \quad (44)$$

where \bar{v} is the mean speed of adsorbed molecules and $f(d = 0)$ is the “frequency” (mol·m⁻¹) with which molecules hit each other inside the pores.

From Eq. (38),

$$f(d = 0) = \frac{1}{l - l_0} = \frac{1}{l_0} \cdot \frac{\theta}{1 - \theta} \quad (45)$$

Therefore, from Eqs. (43), (44) and (45),

$$r_d = N_{pore} \cdot N_{mouth} \cdot \frac{\bar{v} \cdot p(desorb)}{l_0} \cdot \frac{\theta}{1 - \theta} \quad (46)$$

Thus, the initially hidden frequency of desorption can now be represented explicitly,

$$k_d = \frac{\bar{v} \cdot p(desorb)}{l_0} \Leftrightarrow k_d = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (47)$$

given in mol·s⁻¹·mouth⁻¹.

Equating r_a and r_d , multiplying by l_0 on both sides, and solving for bP , it results that,

$$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \quad (48)$$

with,

$$b = \frac{K_H}{n_{max}} \quad (49)$$

and,

$$K_H = \frac{\alpha \cdot A_{mouth} \cdot n_{max}}{k_d \cdot \sqrt{2\pi MRT}} = \frac{\alpha \cdot A_{mouth} \cdot 1/l_0 \cdot L}{k_d \cdot \sqrt{2\pi MRT}} \quad (50)$$

The expression for K_H is, as expected, exactly the same as the one determined for the Langmuir equation. The geometric factor present in K_H for 3D phases, a_0/v_0 , is now $1/l_0$, given that only pore length occupied by the adsorbed molecule influences equilibrium.

Henry Equation for 1D Adsorbed Phases

For 1D adsorbed phases, as in 2D and 3D, the Henry isotherm is obtained, both for localised and distributed adsorption, by considering the effect of low values of θ on the rate of adsorption. In this case, the rate of adsorption is essentially independent of the amount adsorbed, since the probability of a molecule being close to the pore mouth is very small.

Interactions between adsorbed molecules – The Hill-de Boer and Fowler-Guggenheim equations

Adsorbate-adsorbate interactions (so-called “lateral interactions”) cause changes in the heat of adsorption. The activation energy needed to pull an adsorbed molecule away from the surface (or pore) is now the energy associated with interactions between the adsorbed molecule and the surface (or pore) plus the energy associated with the interactions between adsorbed molecules

$$E_a = (-\Delta H)_{ads} = Q_{ads} + (-\Delta H)_{inter} \quad (51)$$

where Q_{ads} represents the energy associated with adsorbate-adsorbent interactions and $(-\Delta H)_{inter}$ represents the energy associated with lateral interactions. $(-\Delta H)_{inter}$ depends on the number of molecules next to each adsorbed molecule, and can therefore be approximated as,

$$(-\Delta H)_{inter} = z \cdot w \cdot \theta \quad (52)$$

where z is the number of positions, adjacent to the molecule, that other molecules can occupy and w is the energy associated with interactions between two adsorbed molecules. θ is equal to the fraction of positions z that are occupied. From Eq. (3), it is possible to write that,

$$k_d = k_0 \cdot \exp\left(-\frac{Q_{ads}}{RT}\right) \cdot \exp\left(-\frac{zw\theta}{RT}\right) \Leftrightarrow k_d = k'_d \cdot \exp\left(-\frac{zw\theta}{RT}\right) \quad (53)$$

Replacing this expression in Eqs. (2), (8), (23), (29) and (46), the desorption rate considering interactions between adsorbed molecules is obtained. The Fowler-Guggenheim and Hill-de Boer equations follow naturally from there,

$$bP = \frac{\theta}{1-\theta} \exp(-c \theta) \quad (54)$$

$$bP = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta}\right) \exp(-c \theta) \quad (55)$$

with,

$$c = \frac{zw}{RT} \quad (56)$$

where c is a system-specific constant.

It should be pointed out that Eq. (51) does not imply that Q_{ads} must be constant regarding θ . In fact, Q_{ads} typically decreases with θ [16, 20], and may actually hide the influence of lateral interactions on the heat of adsorption. If the variation is linear, or can be approximated as such, this dependence can be incorporated into an experimentally determined linearity constant, which would also incorporate, but not be equal to, c . If the variation is not linear, the Fowler-Guggenheim and Hill-de Boer equations (as well as the associated equations of state) do not apply to the system in question.

Conclusions

The Henry, Langmuir, Volmer, Fowler-Guggenheim and Hill-de Boer equations were derived using a kinetic approach. The adsorption systems considered were surfaces (2D adsorbed phase), ultramicropores with single-file diffusion (1D adsorbed phase) and micropores with a radially uniform adsorption potential (3D adsorbed phase). The Kinetic Gas Theory was used as a starting point to determine the rate of adsorption, while the rate of desorption was modelled by considering desorption to be an activated process with an activated energy equal to the heat of adsorption. The exponential term that distinguishes equations for localised and distributed adsorption emerges considering a random distribution of intermolecular distances. This distance influences (in different ways for 1D, 2D and 3D phases) the probability of adsorption occurring upon impact of a gas-phase molecule. Considering localised adsorption in 1D and 2D systems leads to the Langmuir equation. When interactions between adsorbed molecules are considered, through their influence on the heat of adsorption, the Fowler-Guggenheim equation is

obtained. Localised adsorption in 3D adsorption systems was considered to be unrealistic and was not modelled. For distributed adsorption in 1D, 2D and 3D systems, the Volmer isotherm equation was obtained. Incorporating interactions between adsorbed molecules leads to the Hill-de Boer equation. The Henry isotherm can be obtained for 1D, 2D and 3D adsorption phases, from both the Langmuir and the Volmer isotherms, by considering the adsorption rate to be independent from the amount adsorbed. These results are in agreement with those obtained with a thermodynamic approach [7], and show that simple isotherm equations may, in some cases, be applied to micropore adsorption as more than mathematical correlations.

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