Derivation of the BET and Langmuir Isotherms

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1 Langmuir Isotherm

Assumptions used for the Langmuir isotherm

1. Gaseous molecules behave ideally
2. Only one monolayer forms
3. All sites on the surface are equivalent
4. No adsorbate - adsorbate interactions
5. An adsorbed molecule is immobile

Then, for the following reaction

\[ A(g) + S(\text{surface}) \xrightleftharpoons[k_1^{-1}]{k_1} AS(\text{surface}) \]

we can say

rate of adsorption = \( k_1 PN(1-\theta) \)
rate of desorption = \( k_{-1} N \theta \)

where \( P \) is the pressure above the surface, \( N \) is the total number of sites, and

\[ \theta = \frac{\text{number of sites occupied}}{\text{number of sites available}} = \frac{n_a}{n_m} \]

\( n_a \) is the number of molecules adsorbed, and \( n_m \) is the number of molecules in one monolayer. \( N(1-\theta) \) is the number of empty sites and \( N\theta \) is the number of occupied sites.
We can then say that the rate of change of $\theta$ is

$$\frac{d\theta}{dt} = \text{rate of adsorption} - \text{rate of desorption} = k_1PN(1 - \theta) - k_{-1}N\theta$$

At equilibrium $\frac{d\theta}{dt} = 0$ so

$$\theta = \frac{k_1PN}{k_1PN + k_{-1}N} = \frac{KP}{KP + 1}$$

where $K = \frac{k_1}{k_{-1}}$ is the binding equilibrium constant with units of $P^{-1}$.

Figure 1: Langmuir isotherm plot of $n_a/n_m$ vs $P$ (atm) for several different values of the equilibrium binding constant, $K$.

Figure 1 shows a graph of $n_a/n_m$ as a function of pressure in atmospheres for several different values of $K$, the binding equilibrium constant. Figure 2 shows a cartoon representation of how the alumina surface is being filled. For the Langmuir isotherm the alumina surface can be treated as being made of
a bunch of identical slots, each of which can hold one nitrogen molecule. At low pressures the nitrogen molecules begin to fill the slots. As the pressure increases, more nitrogen gets adsorbed as can be seen in the near linear low pressure part of the $n_a/n_m$ vs $P$ curve. As the pressure continues to increase, the slots fill up and eventually the surface is covered. At this point increasing the pressure does not increase the amount of nitrogen adsorbed. This occurs graphically on the flat part of the $n_a/n_m$ vs $P$ curve, where increasing the pressure does not change the amount of nitrogen adsorbed. From this figure we can also see that as the binding equilibrium constant increases (as binding becomes more favorable), the pressure where saturation occurs decreases.

**Langmuir isotherm**

Alumina Surface:
All sites are considered equivalent

Each site can hold one $N_2$ molecule. As $P$ increases the number of molecules adsorbed increases

Once the surface is full, increasing $P$ does not increase the number of molecules adsorbed

Figure 2: Cartoon of nitrogen adsorbing onto an alumina surface assuming a Langmuir isotherm.
2 BET Isotherm

2.1 Assumptions

While the Langmuir isotherm provides a simple picture for looking at surface adsorption, it is not an accurate representation of how nitrogen actually adsorbs to the surface. This is because more than one nitrogen molecule can adsorb to each site on the alumina. A better approximation for this process is to use the BET Isotherm (named for its inventors, Brunauer, Emmett, and Teller) which allows for multiple nitrogen molecules to adsorb to each alumina site.

The assumptions used to derive the BET isotherm are

1. Gaseous molecules behave ideally
2. Multiple nitrogen molecules can be adsorbed to each site
3. Each adsorbed molecule provides a site for the adsorption of the molecule in the layer above it
4. All sites on the surface are equivalent
5. No adsorbate - adsorbate interactions
6. An adsorbed molecule is immobile
7. Nitrogen in the second and higher layers are assumed to be liquid like

2.2 Derivation

Figure 3 shows a cartoon of what an alumina surface would look like under the BET isotherm assumptions. We define $\theta_0, \theta_1, \theta_2, \theta_n...$ where

$$\theta_n = \frac{\# \text{ of sites with } n \text{ adsorbed molecules}}{\# \text{ of sites total}}$$

(Note the definition is the number of sites with n adsorbed molecules, not with “at least” n adsorbed molecules, see Figure 3.) We can also define

$k_n$ - rate of condensation to form the $n^{th}$ layer
$k_{-n}$ - rate of evaporation to form the $n^{th}$ layer
P - pressure above the surface
N - total number of sites
For this cartoon...

\[ q_0 = \frac{3}{14} \]
\[ q_1 = \frac{4}{14} \]
\[ q_2 = \frac{4}{14} \]
\[ q_3 = \frac{2}{14} \]
\[ q_4 = \frac{1}{14} \]

Figure 3: Cartoon of nitrogen adsorbing onto an alumina surface assuming a BET isotherm.

At equilibrium
\[
\frac{d\theta_n}{dt} = 0
\]
for all \( n \). For the bare surface we can write
\[
\frac{d\theta_0}{dt} = rate of evaporation from 1^{st} layer - rate of condensation onto bare surface
\]
\[
\theta_0 = Nk_{-1}\theta_1 - Nk_1P\theta_0
\]
\[
\theta_1 = P\frac{k_1}{k_{-1}}\theta_0
\]

where \( N\theta_1 \) is the number of sites with 1 layer of nitrogen on it and \( N\theta_0 \) is the number of sites with no nitrogen adsorbed. (Note this is the same answer as for the Langmuir isotherm where \( \theta_1 = (1-\theta_0) \).)

For surface sites with only one molecule adsorbed we can write
\[
\frac{d\theta_1}{dt} = \text{rate of condensation onto bare surface} + \text{rate of evaporation from 2nd layer} \\
- \text{rate of condensation onto the 1st layer} - \text{rate of evaporation from the 1st layer} \\
0 = k_1 \theta_0 N + k_{-2} \theta_2 - k_2 P \theta_1 - k_{-1} \theta_1 
\]  
(4)

Combining equations 3 and 4 gives

\[
k_{-2} \theta_2 = k_2 P \theta_1 \\
\theta_2 = P \frac{k_2}{k_{-2}} \theta_1 = P^2 \frac{k_2}{k_{-2}} \frac{k_1}{k_{-1}} \theta_0 
\]  
(5)

For the second layer

\[
\frac{d\theta_2}{dt} = \text{rate of condensation onto 1st layer} + \text{rate of evaporation from 3rd layer} \\
- \text{rate of condensation onto the 2nd layer} - \text{rate of evaporation from the 2nd layer} \\
0 = k_2 \theta_1 N + k_{-3} \theta_3 - k_3 P \theta_2 - k_{-2} \theta_2 
\]  
(6)

Plugging equation 5 into 6 gives

\[
k_{-3} \theta_3 = k_3 P \theta_2 \\
\theta_3 = P \frac{k_3}{k_{-3}} \theta_2 = P^3 \frac{k_3}{k_{-3}} \frac{k_2}{k_{-2}} \frac{k_1}{k_{-1}} \theta_0 
\]  
(7)

Generalizing to the \textit{i}th layer gives

\[
k_{-i} \theta_i = k_i \theta_{i-1} P \\
\theta_i = \frac{k_i}{k_{-i}} P \theta_{i-1} \\
= \frac{k_i}{k_{-i}} \frac{k_{i-1}}{k_{-(i-1)}} \frac{k_{i-2}}{k_{-(i-2)}} \cdots \frac{k_1}{k_{-1}} P^i \theta_0 
\]  
(8)

Since for \( i > 1 \) the BET isotherm assumes the nitrogen is liquid like, we can also say that

\[
k_2 \simeq k_3 \simeq k_4 \simeq k_i \neq k_1 \\
k_{-2} \simeq k_{-3} \simeq k_{-4} \simeq k_{-i} \neq k_{-1}
\]

where \( k_i \) is the rate of adsorption onto a liquid nitrogen surface and \( k_{-i} \) is the rate of desorption off a liquid nitrogen surface. So if we define \( x = P \frac{k_i}{k_{-i}} \), we can write

\[
\theta_i = x^{i-1} P \frac{k_1}{k_{-1}} \theta_0 = x^{i-1} x \frac{1}{P} \frac{k_1}{k_{-1}} \theta_0; i \neq 0, 1 
\]  
(9)
and if we define $c = \frac{P_{k_1}}{x_{k-1}}$, we can say

$$\theta_i = x^i c \theta_0; i \neq 0, 1$$  \hfill (10)

If we then define the total surface coverage, $\theta$, such that

$$\theta = \frac{n_a}{n} = \frac{\text{total \# of molecules adsorbed}}{\text{total \# of sites}}$$

we can write

$$n_a = \sum_{i=0}^{\infty} i \theta_i N$$

because each site has $i$ molecules on it and

$$n = \sum_{i=0}^{\infty} \theta_i N$$

so that

$$\theta = \frac{\sum_{i=0}^{\infty} i \theta_i N}{\sum_{i=0}^{\infty} \theta_i N} = \frac{\sum_{i=1}^{\infty} i \theta_i}{\theta_0 + \sum_{i=1}^{\infty} \theta_i} \frac{c \theta_0 \sum_{i=1}^{\infty} ix^i}{\theta_0 + c \theta_0 \sum_{i=1}^{\infty} x^i}$$

If we use

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x}$$

then

$$\sum_{i=1}^{\infty} ix^i = x \sum_{i=1}^{\infty} ix^{i-1} = x \sum_{i=1}^{\infty} \frac{d}{dx} x^i = x \frac{d}{dx} \sum_{i=1}^{\infty} x^i = x \frac{d}{dx} \frac{x}{1-x} = \frac{x}{(1-x)^2}$$

plugging this in for $\theta$ we obtain

$$\theta = \frac{c \theta_0 \frac{x}{(1-x)^2}}{\theta_0 + c \theta_0 \frac{x}{1-x}} = \frac{c x}{\frac{1}{1-x} + c \frac{x}{(1-x)}} = \frac{c x}{1-x} \frac{1}{1-x + c x} = \frac{c x}{(1-x)(1 + (c-1)x)}$$
2.3 Making Physical Sense of the Constants

The constant $x$ was defined as $x = P(k_i / k_{-i})$ where $k_i$ and $k_{-i}$ are the adsorption rate and desorption rate, respectively, off a liquid nitrogen surface. If we consider a liquid nitrogen surface in equilibrium with the gas state the condition for equilibrium is

$$k_i N P = k_{-i} N$$

or $k_i P = k_{-i}$. The equilibrium pressure for this system, $P$, is just the vapor pressure for pure nitrogen, $P_o$, at the temperature the experiment is being done. Therefore $x$ is just $P / P_o$, the pressure over the equilibrium vapor pressure of liquid nitrogen at the experimental temperature.

The constant $c$ was defined as $(P k_1) / (x k_{-1})$ where $k_1$ is the rate of adsorption onto the bare alumina surface and $k_{-1}$ is the rate of desorption off the surface. Plugging in what we know for $x$, $c$ becomes $(P_o k_1) / (k_{-1})$, a unitless number. Using this and Equation 3, $c = \theta_1 / \theta_0$, the ratio of the number of adsorbed molecules on the first layer to the number of empty sites. This ratio should be

$$c = \frac{n_1}{n_0} = e^{-\frac{\Delta_{des} H^o - \Delta_{vap} H^o}{RT}}$$

where $\Delta_{des} H^o$ is the enthalpy of desorption and $\Delta_{vap} H^o$ is the enthalpy of vaporization. This equation comes about because $n_0$, the number of bare spots, is proportional to $e^{-\frac{\Delta_{des} H^o}{RT}}$ (if desorption is energetically favorable ($\Delta_{des} H^o < 0$) $n_0$ is larger) and the number of molecules in the first monolayer, is proportional to $e^{-\frac{\Delta_{vap} H^o}{RT}}$ (if vaporization is energetically favorable ($\Delta_{vap} H^o < 0$) $n_1$ is larger). Notice that $c$ is large when the enthalpy of desorption from the monolayer is large compared with the enthalpy of vaporization.

2.4 Limitations of the BET Isotherm

The BET isotherm is accurate when $P / P_o$ is between $\sim 0.05$ and $\sim 0.3$, pressures at which only a few complete layers have formed. At low pressures the BET isotherm does not do a good job at describing adsorption because in deriving the isotherm it was assumed that all the sites on the alumina surface are equivalent. This is not really the case and when only a few molecules have adsorbed, effects from inhomogeneities in the surface become more
important. As more molecules adsorb these inhomogeneities average out. At high pressures, the cracks and roughness of the surface cause the BET isotherm to fail. This is especially true for very porous materials where the indents have a width of only a few monolayers. This is because the cracks can only hold a few monolayers and as the cracks fill up, the effective surface area of the solid where the nitrogen adsorbs can change.

3 References


Derivation of the Langmuir and BET Isotherms (http://www.jhu.edu/~chem/fairbr/OLDS/derive.html)


Surface Adsorption (http://chem.colorado.edu/chem4581_91/images/stories/SA.pdf)