Multilayer Adsorption

Equations

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- Empirical isotherm equations
  - BET
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- Summary
All the empirical equations mentioned before are for adsorption with "monolayer" coverage, with the exception of the Freundlich isotherm, which does not have a finite saturation capacity and the DR equation, which is applicable for micropore volume filling.

In the adsorption of sub-critical adsorbates (vapors), molecules first adsorb onto the solid surface as a layering process, and when the pressure is sufficiently high (about 0.1 of the relative pressure) multiple layers are formed.
Brunauer, Emmett and Teller (BET in 1938) are the first to develop a theory to account for this multilayer adsorption, and the range of validity of this theory is approximately between 0.05 and 0.35 of the vapor pressure.

The BET still remains the most important equation for the characterization of mesoporous solids, mainly due to its simplicity.

Edward Teller

- (1908–2003), nuclear physicist born in Budapest, Hungary
- Best Known As: "The Father of the Hydrogen Bomb"

Edward Teller received his Ph.D. in physics from the University of Leipzig (Germany) in 1930.

In Germany during the Weimar years, Teller taught at the University of Göttingen while studying atomic physics under Niels Bohr in Copenhagen.

In 1935 he became Professor of Physics at George Washington University in Washington, D.C.

Teller worked with Enrico Fermi at the University of Chicago to create the first self-sustaining nuclear chain reaction.

In 1943, he was recruited to work with J. Robert Oppenheimer on the fission bomb in Los Alamos, New Mexico. He was active in the research that developed the atomic bomb, first tested in 1952.

From 1954 to 1975 he held top positions at the Lawrence Livermore Laboratory at the University of California at Berkeley.

In the 1980s he was a supporter of Ronald Reagan's Strategic Defense Initiative (Star wars), a protective weapons plan that was ultimately abandoned.

During the 1990s Teller continued to do research and lecture, maintaining his arguments for a strong U.S. defense.
Brunauer, Emmett, Teller model

- Based on Langmuir isotherm
- Monolayer and multilayer adsorption (no limit)
- Layers of adsorbed molecules divided in:
  - First layer with heat of adsorption $\Delta H_{ad,1}$ larger than others.
  - Second and subsequent layers with $\Delta H_{ad,2} = \Delta_{Condensation}$

\[
\frac{(k_a)_i}{(k_d)_i} = \alpha \quad ; \quad \text{for} \quad i = 2, 3, \ldots
\]
Multiple layering in BET theory

$s_0$, $s_1$, $s_2$ and $s_n$ are the surface areas covered by no layer, one layer, two layers and $n$ layers of adsorbate molecules.

$V_i$: the volume of gas adsorbed on the section of the surface having "$i" layers.

Langmuir assumption:

$$a_i P s_{i-1} = b_i s_i \exp \left( \frac{-E_i}{R_g T} \right)$$

$$S = \sum_{i=0}^{\infty} s_i$$

$$V_i = V_m \left( \frac{is_i}{S} \right)$$
BET Model

For every layer
- 1st layer
- n\textsuperscript{th} layer

Langmuir model

\[ \sum \theta_i = 1 \]

\[ n_{ad} = n_m (\theta_0 + 2\theta_1 + 3\theta_2 + \ldots) \]

\[ k_d^0 \theta_0 p = k_d^1 \theta_1 \]

\[ k_d^{n-1} \theta_{n-1} p = k_d^n \theta_n \]

\[ \theta_1 = \frac{k_d^0}{k_d^1} p \quad \theta_0 = K_1 p \quad \theta_0 \]

\[ \theta_n = \frac{k_d^0}{k_d^n} p \quad \theta_{n-1} = K_n p \quad \theta_{n-1} \]
BET Model

Assume

\[ K_1 = K_{1,0} e^{\frac{\Delta H_{ads}}{RT}} \]

\[ K_n = K_{n,0} e^{\frac{\Delta H_n}{RT}} \approx K_{n,0} e^{\frac{\Delta H_{cond}}{RT}} \]

\[
\frac{n_{ad}}{n_m} = \frac{C}{\left(1 - \frac{p}{p^0}\right) \left(1 + (C - 1) \frac{p}{p^0}\right)} \frac{p}{p^0}
\]
BET equation

The famous form of BET equation containing two fitting parameters, $C$ and $V_m$ is:

$$\frac{V}{V_m} = \frac{C P}{(P_0 - P)[1 + (C - 1)(P / P_0)]}$$

$$C = \exp\left(\frac{\Delta H_{ad} - \Delta H_{cond}}{RT}\right)$$
BET equation does not fit entire adsorption isotherm.

Different mechanisms play a role at low and at high $P$.

C is a constant parameter and usually very large (100-1000).

BET ‘C’ constant varies from solid to solid. Low values represent weak gas adsorption typical of low surface area solids, organics and metals in particular.

The larger is the value of C, the sooner will the multilayer form and convexity of the isotherm increases toward the low pressure range.
Other forms of BET equation

\[ \frac{V}{V_m} = \frac{C (P/P_0)}{(1 - P/P_0)[1 + (C - 1)(P/P_0)]} \]

*Linearized form:*

\[ \frac{1}{V [(P_0/P - 1)]} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \left( \frac{P}{P_0} \right) \]
Differential heat

The isosteric heat of the BET isotherm is obtained from the following equation:

\[- \Delta H = E_L + q \frac{(1 - \frac{P}{P_0})^2}{1 + (C - 1)\left(\frac{P}{P_0}\right)^2}\]

\[q = -R_g T^2 \left(\frac{\partial \ln C}{\partial T}\right)_\theta\]

q is the difference between the energy of adsorption of the first layer and the heat of liquefaction.
Surface area determination
Surface Area – What is it?

“Surface Area is the means through which a solid interacts with its surroundings, especially liquids and gases.”

Surface Area affects reaction rates with liquids and gases, e.g. dissolution, adsorption, catalytic activity.

Surface area is created by division of particles (size reduction) and the generation of porosity.

Surface area is destroyed by sintering (exceeding $T_g$), melting, etc.
How to Create Area

- Size Reduction
  - Grinding,
  - milling,
  - nanoscale preparation

- Make pores
  - Partial decomposition
  - Leaching
  - Gelling then freeze drying
Suitable Methods of Determination

- Gas adsorption allows probing of entire surface including irregularities and pore interiors.

- The amount adsorbed is a function of temperature, pressure and the strength of attraction or interaction potential.

- Physisorption is generally weak and reversible. The solid must be cooled and a method used to estimate the monolayer coverage from which surface area can be calculated.
Principles of BET Surface Area Measurement and Calculation

- BET equation is used extensively for the surface area determination because once the monolayer coverage $V_m$ and the area occupied by one molecule is known the surface area of the solid can be calculated.

- To conveniently determine $V_m$, the linear form of BET equation is used:

$$\frac{P}{V \left( P_0 - P \right)} = \frac{1}{V_m \cdot C} + \left( \frac{C - 1}{V_m \cdot C} \right) \frac{P}{P_0}$$

Slope $= \frac{(C - 1)}{CV_m}$

Intercept $= \frac{1}{CV_m}$
Once $V_m$ (mole/g) is obtained from the slope, the surface area is calculated from:

\[ A = V_m N_A a_m \]

$N_A$ : the Avogadro number

$a_m$ : the molecular projected area.
# Molecular Projected Area of some common gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (K)</th>
<th>$P_0$ (Pa)</th>
<th>$a_m$ ($\text{A}^2$/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>argon</td>
<td>77</td>
<td>$2.78 \times 10^4$</td>
<td>15</td>
</tr>
<tr>
<td>ammonia</td>
<td>209</td>
<td></td>
<td>12.6</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>195</td>
<td>$1.013 \times 10^5$</td>
<td>20</td>
</tr>
<tr>
<td>n-butane</td>
<td>273</td>
<td>$1.013 \times 10^5$</td>
<td>44</td>
</tr>
<tr>
<td>krypton</td>
<td>90</td>
<td>$2.74 \times 10^3$</td>
<td>20</td>
</tr>
<tr>
<td>methane</td>
<td>90</td>
<td>$1.08 \times 10^4$</td>
<td>16</td>
</tr>
<tr>
<td>nitrogen</td>
<td>77</td>
<td>$1.013 \times 10^5$</td>
<td>16</td>
</tr>
<tr>
<td>oxygen</td>
<td>79</td>
<td></td>
<td>14.1</td>
</tr>
<tr>
<td>sulfur dioxide</td>
<td>250</td>
<td></td>
<td>18.7</td>
</tr>
<tr>
<td>xenon</td>
<td>90</td>
<td>8.25</td>
<td>23</td>
</tr>
</tbody>
</table>
Choice of Gas and Temperature

- **Gases**
  - Nitrogen
  - Argon
  - Krypton
  - Carbon dioxide
  - Others

- **Temperatures**
  - Liquid Nitrogen
  - Liquid Argon
  - Dry ice/acetone
  - Water/ice
  - Others
Cont.

- Adsorbate most commonly used is nitrogen.
  - Readily available in high purity
  - Appropriate coolant, liquid nitrogen, also plentiful.
  - Gas-solid interaction relatively strong.
  - Widely accepted cross sectional area (16.2Å²).
**Measurement**

- Obtain at least three data points in the relative pressure range:
  
  0.05 to 0.30

- Plot $1/[V_{\text{STP}}(P_o/P)-1]$ or $P/[V(P_o-P)]$ *versus* $P/P_o$. It should yield a straight line... if the BET model holds true.

- On all surfaces the BET model fails to accurately predict the multilayer adsorption behavior above $P/P_o = 0.5$ (the onset of *capillary condensation* which fills pores with liquid adsorbate).
Limitation

- The BET equation is able to describe type I, II and III isotherms.

- One of the assumptions of the BET theory is the allowance for infinite layers of molecules to build up on top of the surface. In the last two isotherm types, there is a limited number of layers formed above the solid surface.
Measurement Method

Manometric
(Classical vacuum, volumetric.)

Requires that adsorbate be adsorbed by the sample, at some reduced temperature, as a function of pressure of pure adsorptive.
Manometric

calibration chamber
dosing manifold transducer
sample cell transducer
dilution gas
N2
He
vacuum
Working Equation

\[ PV = nRT \]

\[ n_{ads} = n_{dosed} - n_{void} \]

\[ n_{ads} = \left( \frac{\Delta PV}{RT} \right)_{\text{man.}} - \left( \frac{PV}{RT} \right)_{\text{cell}} \]
Working Equation

\[ n_{ads} = (\Delta PV/RT)_{\text{man.}} - (PV/RT)_{\text{cell}} \]

That means, the amount adsorbed is calculated as the difference between:

a) the amount of gas “dosed” from the manifold to the cell and
b) the mount of gas which remains not adsorbed at the end of the “equilibration time”.

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- Measure surface area and pore size of up to 3 samples simultaneously.
- Autosorb-3B equipped with three built-in degas ports.
The Gas Adsorption Isotherm

Amount adsorbed, $V$

Relative pressure, $P/P_o$
Calculation of Surface Area by BET method

\[ V \left( P_o - P \right) \]

relative pressure, \( P/P_o \)

*negative* intercepts are unacceptable
Calculation

Fit best straight line through BET data set using least squares regression to find:

\[
\text{slope } \quad s = \frac{C - 1}{V_m C}
\]

\[
\text{intercept } \quad i = \frac{1}{V_m C}
\]
Solving for \( V_m \)

\[
V_m = \frac{1}{s + i}
\]

Total surface area, \( S_t \), is calculated thus:

\[
S_t = \frac{V_m N_{av} A_m}{M_v}
\]

\[
N_{av} = 6.022 \times 10^{23}
\]

\[
A_m = 0.162 \text{ nm}^2
\]

\[
M_v = 22414 \text{ mL}
\]
Example

\[ V_m = 4 \text{ mmol/g} \]

\[ S_g = 809 \frac{\text{m}^2}{\text{g}} \]

\[ \text{Slope} = \frac{(C - 1)}{CV_m} = 0.2493 \]

\[ \text{Intercept} = \frac{1}{CV_m} = 1.188 \times 10^{-3} \]
Calculation of Surface Area by BET method

visual check for linearity

\[ V(P_0 - P) \] against relative pressure, \( P/P_0 \)

negative intercepts are unacceptable
Multi-Point BET Plot (Interpretation)

- Never use data points too low in relative pressure ($P/P_o$).
- Never use data points too high in ($P/P_o$).
Multi-Point BET Plot (Interpretation)

- Discard under-equilibrated points (at low $P/P_0$)
- Never use less than three, preferably five data points.

![Graph of Multi-Point BET Plot](image)
Single-point BET Method

- Set intercept to zero, i.e. ignore ‘C’ (adsorption strength)
- Monolayer volume is inverse of slope.
- $P/P_0 = 0.3$ gives good general agreement with multi-point – the higher the C value, the better the agreement.
  (note: monolayer is formed closer to $P/P_0 = 0.2$)

Approximate values of C

- $C = 2$ to $50$ metals, polymers, organics
- $C = 50$ to $200$ oxides, silicates
- $C = >200$ activated carbons, zeolites
Calculation of Surface Area by single point BET method

\[ P \]  

\[ V(P_0 - P) \]  

relative pressure, \( P/P_o \)
Other Uses of the Single-point Method

To determine appropriate $P/P_0$ range for multi-point BET.

- Acquire minimum seven data points in the $P/P_0$ range 0.05 to 0.3.
- Discard *objectively* from the multipoint surface area calculation those higher $P/P_0$ values that clearly do not lie on a straight BET line.
- The upper limit of the linear BET range can usually be obtained by calculating the single-point BET area using each data point in turn. Normally, the calculated single-point area will increase with increasing $P/P_0$ up to some maximum, beyond which the calculated value will decrease. That maximum indicates the upper limit for the multi-point range.
Standard Surface Area Method

- Static Volumetric Apparatus
  Multi-point BET
  Correlation coefficient, $r > 0.9975$

- Dynamic Flow Apparatus
  Single-point BET

- Krypton for very low surface areas
  ($< 0.5 \, \text{m}^2/\text{g}$)
BDDT (Brunauer, Deming, Deming, Teller) Classification
The theory of BET was developed to describe the multilayer adsorption.

Adsorption in real solids has given rise to isotherms exhibiting many different shapes. However, five isotherm shapes were identified (Brunauer et al., 1940).

The following five systems typify the five classes of isotherm.

- **Type 1**: Adsorption of oxygen on charcoal at -183 °C
- **Type 2**: Adsorption of nitrogen on iron catalysts at -195°C (many solids fall into this type).
- **Type 3**: Adsorption of bromine on silica gel at 79°C, water on glass
- **Type 4**: Adsorption of benzene on ferric oxide gel at 50°C
- **Type 5**: Adsorption of water on charcoal at 100°C
Very Low Pressure Behavior
(micropore filling)
Low Pressure Behavior (monolayer)

The “knee”

Amount Adsorbed vs Relative Pressure, $P/Po$
Medium Pressure Behavior (multilayer)
High Pressure Behavior (capillary condensation)
Types of Isotherms

- **Type I or pseudo-“Langmuir”**
  - Steep initial region due to very strong adsorption, for example in micropores.
  - Limiting value (plateau) due to filled pores and essentially zero external area.
Types of Isotherms

Type II

Absence of hysteresis indicates adsorption on and desorption from a non-porous surface.

Low slope region in middle of isotherm indicates first few multilayers.

Rounded knee indicates approximate location of monolayer formation.

Volume adsorbed

Relative Pressure ($P/P_0$)
Types of Isotherms

**Type III**

Lack of knee represents extremely weak adsorbate-adsorbent interaction

Example: krypton on polymethylmethacrylate
Types of Isotherms

**Type IV**

Closure at $P/P_o \sim 0.4$ indicates presence of small mesopores (hysteresis would stay open longer but for the tensile-strength-failure of the nitrogen meniscus).

Rounded knee indicates approximate location of monolayer formation.

Hysteresis indicates capillary condensation in meso and macropores.

Low slope region in middle of isotherm indicates first few multilayers

BET is not applicable
Types of Isotherms

Type V

Lack of knee represents extremely weak adsorbate-adsorbent interaction
BET is not applicable

Example: water on carbon black

Volume adsorbed

Relative Pressure (P/P₀)
BET Equation for n-Layers

- When the adsorption space is finite which is the case in pores of finite size (i.e. the adsorption layer is limited by n), the resulting n-layer BET equation will take the form:

\[
\frac{V}{V_m} = \frac{Cx}{1-x} \frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (C - 1)x - Cx^{n+1}}
\]

\[x = \frac{P}{P_0}\]
Cont.

- When \( n \) approaches infinity, this equation reduces to the classical BET equation.
- When \( n = 1 \), we have the famous Langmuir equation.
- When the pressure approaches the vapor pressure, it reduces to:

\[
\lim_{{x \to 1}} \frac{V}{V_m} = \frac{n(n + 1)C}{2(nC + 1)}
\]
Other equations for multilayer adsorption

- Aranovich's modified BET equation
- Anderson isotherm
- Harkins-Jura isotherm
- Halsey isotherm
- Frenkel, Halsey and Hill (FHH) multilayer equation
- Redhead's empirical isotherm

Despite the improvement of some equations over the original BET equation, it is still the most popular equation used because of its simplicity.
### Summary of Multilayer adsorption isotherm equation

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Expression</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>( \frac{V}{V_m} = \frac{C x}{(1-x)[1+(C-1)x]} )</td>
<td>( V_m, C )</td>
</tr>
<tr>
<td>n-layers BET</td>
<td>( \frac{V}{V_m} = \frac{C x (1-(n+1)x^n + nx^{n+1})}{1-x(1+(C-1)x - Cx^{n+1})} )</td>
<td>( V_m, C, n )</td>
</tr>
<tr>
<td>Langmuir case VI</td>
<td>( \frac{V}{V_m} = \frac{C k x}{(1-kx)[1+(C-1)kx]} )</td>
<td>( V_m, C, k )</td>
</tr>
<tr>
<td>Anderson</td>
<td>( \frac{V}{V_m} = \frac{C x}{(1-jx)[1+(C-1)x]} )</td>
<td>( V_m, C, j )</td>
</tr>
<tr>
<td>Anderson</td>
<td>( \frac{V}{V_m} = \frac{C k x}{(1-jkx)[1+(C-1)kx]} )</td>
<td>( V_m, C, j, k )</td>
</tr>
<tr>
<td>Aranovich</td>
<td>( \frac{V}{V_m} = \frac{C x}{\sqrt{1-x(1+Cx)}} )</td>
<td>( V_m, C )</td>
</tr>
<tr>
<td>Harkins-Jura</td>
<td>( \ln(x) = B - \frac{C}{V^2} )</td>
<td>( B, C )</td>
</tr>
<tr>
<td>FHH</td>
<td>( \ln(x) = -A(V)^{-B} )</td>
<td>( A, B )</td>
</tr>
<tr>
<td>Redhead</td>
<td>( \frac{V}{V_m} = \left[ \frac{(2n-1)x}{1-x} \right]^{1/n} )</td>
<td>( V_m, n )</td>
</tr>
</tbody>
</table>

\[ x = \frac{p}{P_0} \]


Particle Size Measurement Vols 1 & 2 by Terence Allen 5th edition (1997), Springer (2 volume set)

Particle Characterization: Light Scattering Methods by Ren Xu (2000), Springer

Particle-Particle Adhesion in Pharmaceutical Powder Handling by Fridrun Podczeck (1999), World Scientific Publishing Company