Adsorption

December 2014
Nanosized objects have a large surface area

Dividing the size of an object by 2...

... doubles the accessible surface
Adsorption ≠ Absorption

Absorption is a phenomenon that occurs in a volume

Adsorption is a phenomenon that occurs on a surface

The word sorption encompasses both types of phenomena
Adsorption of methylene blue from bentonite

https://www.youtube.com/watch?v=3xDjTEv9D1o
Applications of adsorption
Making charcoal at the Jack Daniel Distillery, ca. 1920-1935
Estimate an order of magnitude of the specific surface area of carbon blacks
Orders of magnitude

Figure: 1kg of active carbon has a surface of about $10^6$ m$^2$, i.e. $10^{26}$ A$^2$;

One generally assumes that a molecule of nitrogen occupies a surface of about 16 A$^2$;

The total number of molecules needed to cover the surface of 1 kg of carbon black is therefore roughly 10 mol;

This is 220 l of gas STP i.e. the volume of 22 buckets of gas
Adsorption isotherm (liquid phase)

Amount adsorbed vs concentration

Chemical potential

Dye adsorption in peat
N molecules adsorb on a surface with a total of A adsorption sites. The binding energy per molecule is \( u \).

What is the chemical potential of an adsorbed molecule?
The Langmuir model

Figure VIII–3: On a given surface with $A$ adsorption sites, there are a) $\Omega_1 = A$ different configurations with $N = 1$ molecules, b) $\Omega_2 = A \times (A - 1)/2$ configurations with 2 molecules, and c) in general $\Omega = \binom{A}{N}$ for $N$ adsorbed molecules.

$$S = k_B \ln(\Omega)$$

$$\Omega = \binom{A}{N} = \frac{A!}{N!(A - N)!}$$
Chemical potential of adsorbed species

\[ \mu_{ads} = u_a + k_B T \ln \left[ \frac{N}{A - N} \right] \]
Gas-phase Adsorption Measurement (volumetric device)

gas inlet (adsorption)

To vacuum (desorption)

valve

valve

pressure gauges

P

calibrated piston

thermostat (liquid nitrogen)

sample
Building up the isotherm

The pressure decrease following each piston injection results from the adsorption of a measurable quantity of gas.

The adsorption isotherm is obtained by plotting the cumulated quantity adsorbed against the equilibrium pressure.
A rule of thumb

The lowest surface you can accurately measure with nitrogen adsorption on a volumetric device is 20 m².

That figure can be reduced to, say 1 m² if an adsorbate with lower condensation pressure is used (e.g. 2 mm Hg for Kr at 77K).

In the case of silica spheres, the surface to volume

\[
\frac{S}{m} = \frac{6}{2 \times 10^6 [g/m^3] d [nm]}
\]

For a sample of about 1g, the largest measurable particle is about 100 nm across.
Gas-phase adsorption

Figure VIII–9: Example of nitrogen adsorption at 77 K measured on a carbon nanotubes sample. Note the different shape with respect to the type I isotherms described by Langmuir’s equation.
Adsorption-desorption isotherm

Surface phenomena

Pore-filling phenomena

Chemical potential
Adsorption Lexicon

- Adsorbent: The solid itself (e.g. carbon black, silica, etc.);
- Adsorbate: The adsorbed gas (e.g. nitrogen, krypton, argon, etc.);
- Mesopore: A pore having a size from 2 nm to 50 nm;
- Micropore: A pore smaller than 2 nm;
- Macropore: A pore larger than 50 nm.
INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON COLLOID AND SURFACE CHEMISTRY*
Subcommittee on Characterization of Porous Solids

RECOMMENDATIONS FOR THE
CHARACTERIZATION OF POROUS SOLIDS
(Technical Report)

Prepared for publication by the Subcommittee
on Characterization of Porous Solids, consisting of

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K. S. W. SING (UK) and K. K. UNGER (FRG).
The 6 types of isotherms according to the IUPAC classification

I: microporous solids

II & III: multilayer adsorption in non-porous solids

IV & V: capillary condensation in mesoporous solids

VI: stepped adsorption
Type II & III isotherms: multilayer adsorption on non-porous solids

Progressive adsorption with no hysteresis

Nitrogen on closed MWCNTs
Multilayer adsorption
the BET equation (1938)

From I. Hargittai,
The Martians of Science
Oxford University Press

Left: The three scientists of the B.E.T. equation, Paul Emmett, Stephen Brunauer, and Edward Teller, on the occasion of a later reunion. (Courtesy of Wendy Teller and Paul Teller.)
The BET equation

The assumptions of the BET equation are:

1) Adsorption occurs layer by layer;
2) Molecules in the first layer interact with the solid & molecules in the following layers behave as in bulk liquid;
3) Lateral interactions between adsorbed molecules are neglected.

\[ W = W_0 \left( \frac{C \frac{P}{P_0}}{1 - \frac{P}{P_0}} \left(1 + \frac{(C - 1)P}{P_0} \right) \right) \]

where \( W \) is the amount adsorbed at pressure \( P \), \( W_0 \) is the amount needed to cover the total surface with a monomolecular layer (or monolayer), and \( C \) is a parameter related to the energy of interaction between the adsorbent and adsorbate.
BET adsorption isotherms
The equation is rearranged as

\[ \frac{P / P_0}{W(1 - P / P_0)} = \frac{1}{CW_0} + \frac{C - 1}{CW_0} P / P_0 \]

When the left-hand-side is plotted against \( P/P_0 \), a straight line is expected, which enables to determine \( W_0 \) and \( C \).

The volume of the monolayer is converted to a specific surface area \( S \) by assuming that each molecule in the monolayer occupies a given surface (16.2 A\(^2\) for nitrogen).
Examples of BET plots

A « real » non-porous solid

A mesoporous solid

A microporous solid