EXPERIMENTAL METHODS IN COLLOIDS AND SURFACES

PARTICLE SURFACE AREA FROM GAS ADSORPTION
TYPES OF ADSORPTION

- Physical adsorption: rapid, depends on adsorbate bulk concentration, multiple molecular layers may adsorb, increases at lower temperatures, nonspecific sites, reversible process

- Chemisorption: very specific adsorption sites, usually limited to a monolayer, increases with temperature
ADSORPTION APPLICATIONS

- Adsorbent: solid substrate on which the gas is adsorbed
- Adsorbate: the adsorbing gas
- Adsorbents are used to purify air and water, as catalysts, for color and odor removal, dehydration, separations
ADSORPTION ISOTHERMS

- Langmuir isotherm: adsorption increases linearly with adsorbate bulk.
- At a maximum saturation level, the amount of adsorbate adsorbed on the surface remains constant.
- Maximum saturation means monolayer coverage.
LANGMUIR ISOTHERM

- Type I Isotherm

Amount Adsorbed

Adsorbate bulk concentration
LANGMUIR ISOTHERM

Main assumptions:

- Energy of adsorption is uniform
- Adsorption rate proportional to bulk concentration and number of vacant sites
- Desorption rate proportional to number of molecules on the surface
LANGMUIR ISOTHERM

- Adsorption rate = $k_A (1-f) C$
- Desorption rate = $k_D f$
- At equilibrium, rates are equal
  
  $$k_A (1-f) C = k_D f$$

  $$f = \frac{(bC)}{(1 + bC)}$$

  $b = \frac{k_D}{k_A}$; $C$ = adsorbate bulk concentration; $f$ is fraction of sites covered by adsorbate
LANGMUIR ISOTHERM

- Plot $C/f$ versus $C$ --get a straight line if the Langmuir model is valid for the data
- The monolayer adsorption value is determined as $1/$slope of the plot of $C/f$ versus $C$. 
ADSORPTION ISOTHERMS

- With gas adsorption—often multilayers of gas adsorb rather than a single monolayer.
- Brunauer classified adsorption isotherms into five types (with Langmuir as Type I)
- Brunauer, Emmett and Teller (BET) extended the Langmuir model to multilayer adsorption
- Physical adsorption may include mono and multilayer adsorption, condensation in pores or capillaries
Multilayer Physical Adsorption on nonporous solids: Type II isotherm

Volume adsorbed

Monolayer coverage, $V_m$

pressure

Approaching saturated vapor pressure
POWDER SURFACE AREA

- Powder surface area is determined using physical adsorption of an inert gas, such as nitrogen. Adsorption proceeds as in the Type II isotherm.
- BET method is used since the model fits experimental data very well.
BET Equation

\[
\frac{1}{V} \left( \frac{x}{1-x} \right) = \frac{c-1}{cV_m} \cdot x + \frac{1}{cV_m}
\]

\(V\) = volume of gas adsorbed
\(V_m\) = volume of gas adsorbed at monolayer coverage
\(X = P/P_o\)
\(c = \exp \left( \frac{e-e_v}{kT} \right)\)
BET Equation

- A plot of \( \frac{1}{V} \frac{x}{(1-x)} \) versus \( x \) gives a straight line with
  
  slope = \( m = \frac{(c-1)}{(cV_m)} \)
  
  intercept = \( b = \frac{1}{cV_m} \)

Solve to get \( V_m \) and \( c \)

\( V_m = \frac{1}{(\text{slope} + \text{intercept})} \)
BET Equation

- Adsorption model fits experimental data well for nonporous solids
- It is linear in the pressure range from 0.05 $p_o$ to 0.35 $p_o$
- Adsorbate used is nitrogen at 77K (liquid nitrogen)
- Area per molecule is 16.2 square Angstroms
BET Equation

- Other adsorbates may be used, provided the surface area is well known and the molecular configuration on the surface does not vary.
- Cross sectional areas of molecules adsorbed on surfaces is given in McClellan, A.L. and Harnsberger, H.F., J. Colloid Interface Sci., \textbf{23}, 577 (1967).
BET Equation Limit

- If $c$ is large and $x$ is small, the BET equation reduces to the Langmuir equation.
Specific Surface Area

The specific surface area, $A_{sp}$ can be calculated from the results of BET measurements:

$$A_{sp} = \frac{S_t}{W} = \frac{\text{total surface area}}{\text{weight of powder sample}}$$
Specific Surface Area

Total surface area, $S_t$ is

\[(A/A_c) \cdot V_c \cdot (P_a M_a / RT) \cdot (1 - P/P_o)\]

Where

$A = \text{sample integrator reading}$

$A_c = \text{calibration integrator reading}$

$V_c = \text{calibration volume}$

$P_a = \text{ambient pressure}; \ P_o \text{ is total pressure}$

$T = \text{temperature, } R, \text{ gas constant}$

$M_a = \text{adsorbate molecular weight}$
Single Point BET Method

- Often the single point method is used, since the intercept of the BET plot is small compared to the slope; there is little error in this method compared to a multipoint analysis.
- In this case, the experimental point measured must be very close to \( P/P_0 = 0.30 \).
Lab Experiment

In the lab, we will measure the surface area of an alumina powder using the multipoint and single point BET methods.