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

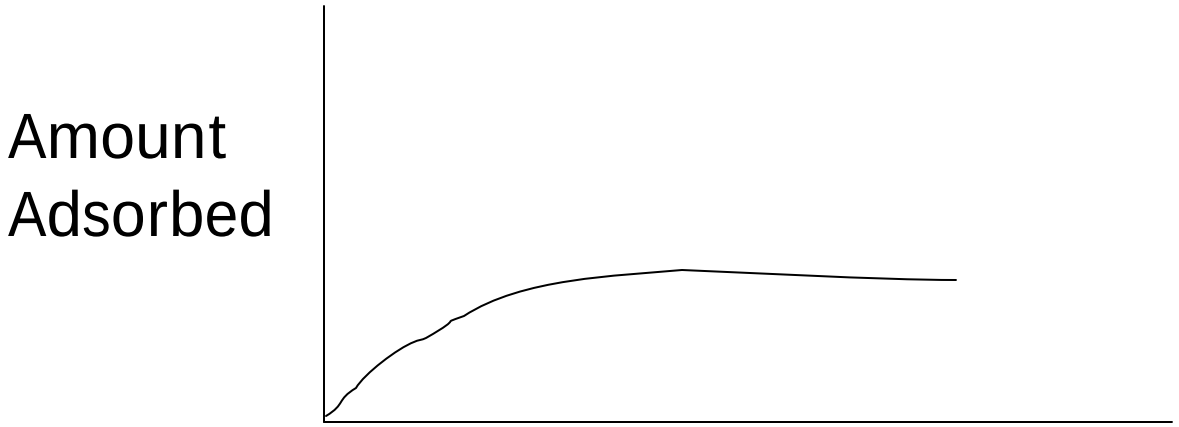
- Adsorbent: solid substrate on which the gas is adsorbed
- Adsorbate: the adsorbing gas
- Adsorbents are used to purify air and water, as catalysts, for color and odor removal, dehydration, separations

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



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

$$k_A(1-f)\ C = k_D\ f$$

$$f = (bC)/(1 + bC)$$

$b = k_D/k_A$; C = adsorbate bulk concentration; f is fraction of sites covered by adsorbate

LANGMUIR ISOTHERM

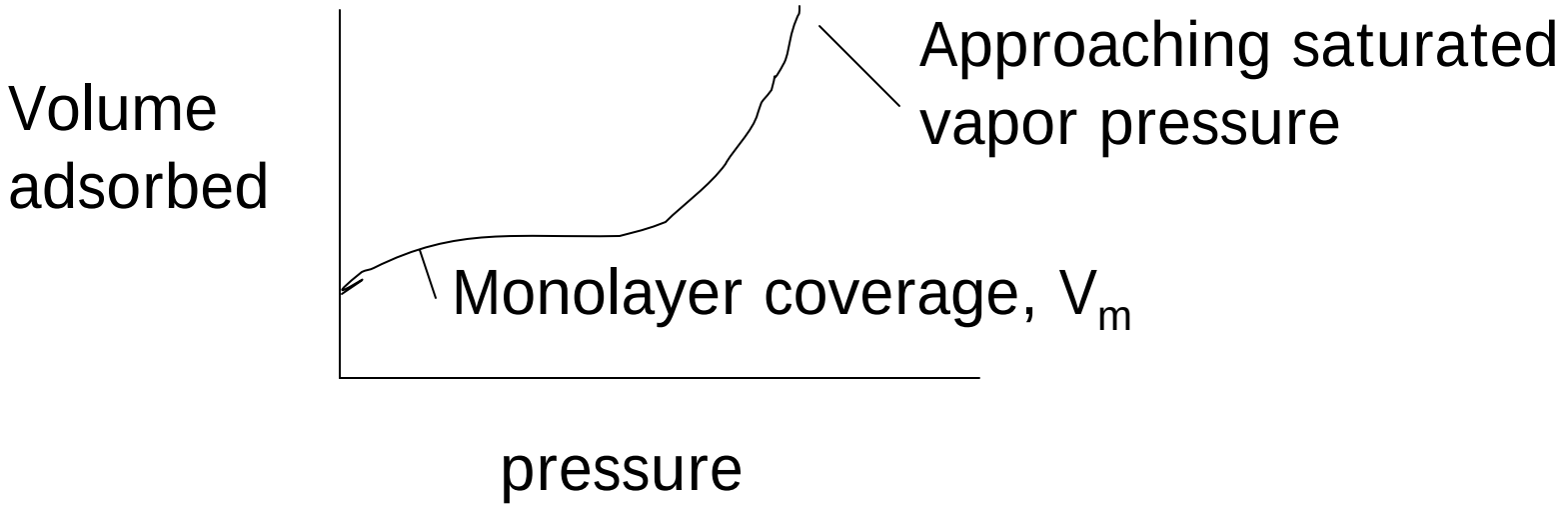
- Plot C/f versus C --get a straight line if the Langmuir model is valid for the data
- The monolayer adsorption value is determined as 1/slope of the plot of C/f versus C.

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

BET ISOTHERM

Multilayer Physical Adsorption on nonporous solids: Type II isotherm



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

$$(1/V)(x/(1-x)) =)(c-1)/cV_m) x + 1/cV_m$$

V = volume of gas adsorbed

V_m = volume of gas adsorbed at monolayer coverage

$X = P/P_o$

$c = \exp((e-e_v)/kT)$

BET Equation

- A plot of (1/V)(x/(1-x)) versus x gives a straight line with

slope = m= (c-1)/(cV_m)

intercept = b= 1/cV_m

Solve to get V_m and c

Vm = 1/(slope + 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., **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:

Asp = S_t/W

= total surface area/weight of powder sample

Specific Surface Area

Total surface area, S_t is

$(A/A_c)\ V_c\ (P_aM_a/RT)\ (1-P/P_o)$

Where

A = sample integrator reading

A_c = calibration integrator reading

V_c = calibration volume

P_a = ambient pressure; P_o is total pressure

T = temperature, R, gas constant

M_a = 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

  $P/Po = 0.30$

Lab Experiment

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