

Adsorption

At the Solid-gas interface

Gas molecules + Clean Solid Surface → Adsorption

Why?

To balance the excess E_{free} on the surface of the solid.

What is the difference between solid and liquid surfaces?

Adsorption process

Adsorbent (referred to the solid)

Adsorbate (adsorbed gas)

Adsorptive (non-adsorbed gas)

Adsorption process

- **Any solid (metal, ceramic, metal oxides, charcoal,..etc.,) is capable of adsorbing a certain amount of gas.**
- **The extent of adsorption at equilibrium depending on Temperature, Pressure and effective surface area.**
- **Adsorption reduces the imbalance of attractive forces which exists at a surface, and hence, the surface free energy of a heterogeneous system.**

Adsorption isotherm

Adsorption isotherm: *The relationship at constant temperature between the equilibrium adsorbed amount of gas adsorbed and the pressure of the gas.*

- **Molecules and atoms can attach to surfaces in two ways: Physisorption or chemisorption**

Physisorption

- *Physisorption*: Physical adsorption.
- There is a van der Waals interaction (dispersion or dipolar interaction) between the adsorbate and the substrate.
- The energy released is of the same order of magnitude as the enthalpy of condensation.
- The enthalpy of physisorption (measured by monitoring the rise in temperature of a sample of known heat capacity) typical values are in the region of 20kJmol^{-1}

Chemisorption

- ***Chemisorption: chemical adsorption***
- **The molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond, and tend to find sites that maximize their coordination number with the substrate.**
- **Enthalpy is about 200 kJmol^{-1} .**
- **The distance between the surface and the closest adsorbate is shorter for chemisorption.**
- **Chemisorption must be exothermic (in most cases).**

Thermodynamic Consideration

A spontaneous process requires $\Delta G < 0$.

ΔS is negative for the adsorbate.

Therefore, from

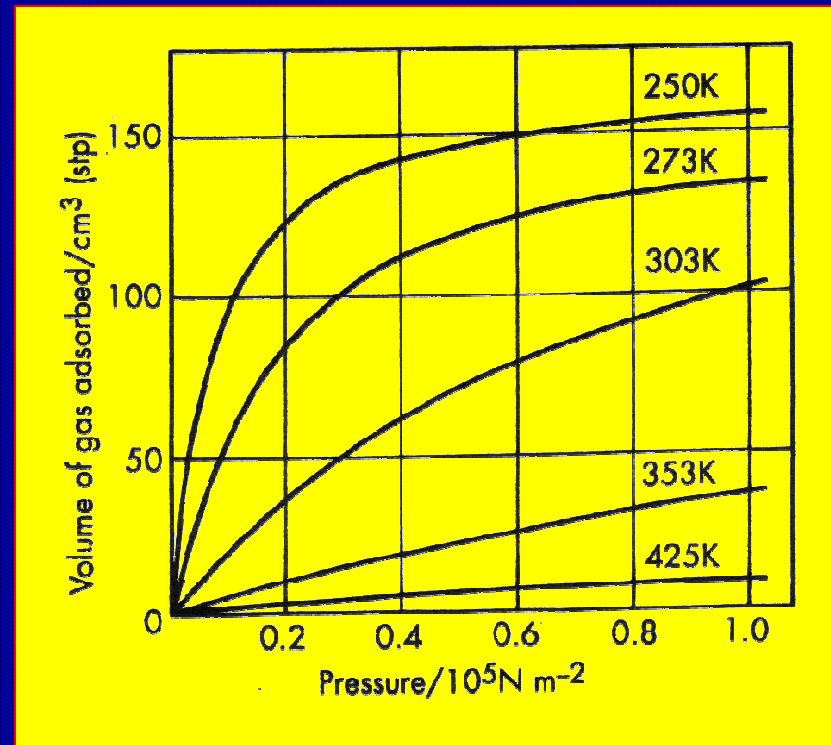
$$\Delta G = \Delta H - T\Delta S$$

\therefore in order for ΔG be negative,

ΔH must be negative

i.e. the process should be exothermic and the degree of adsorption increases with decreasing temperature (Figure 1)

Thermodynamic Consideration

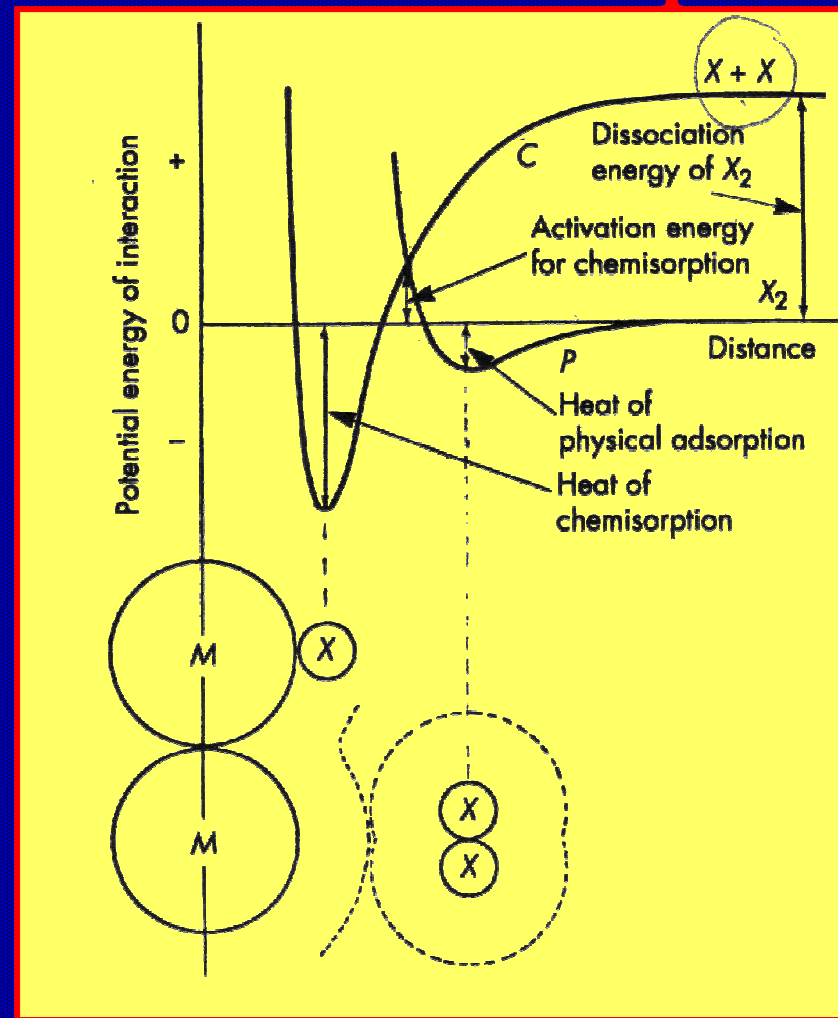


The degree of adsorption increases with decreasing temperature (Figure 1)

Thermodynamic Consideration

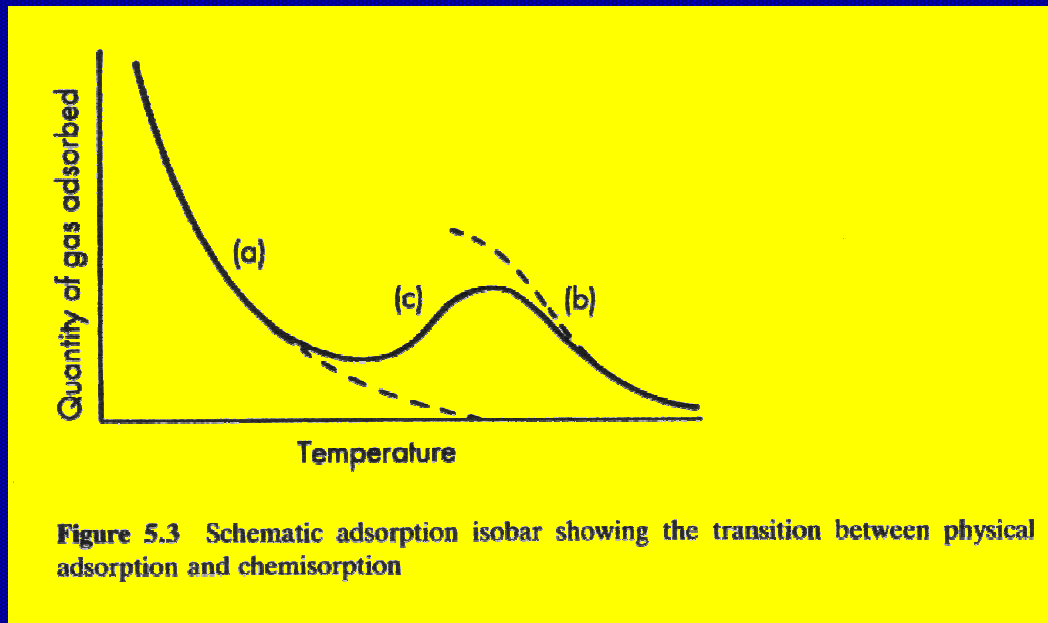
- The principal test for distinguishing chemisorption from physisorption used to be the enthalpy of adsorption.
- Enthalpy of physisorption of gases are usually similar to their heats of condensation ($< 20 \text{ KJmol}^{-1}$).
- Enthalpy of Chemisorption of gases are much larger ($40 - 400 \text{ KJmol}^{-1}$).

The Nature of the Physical adsorption and Chemical adsorption

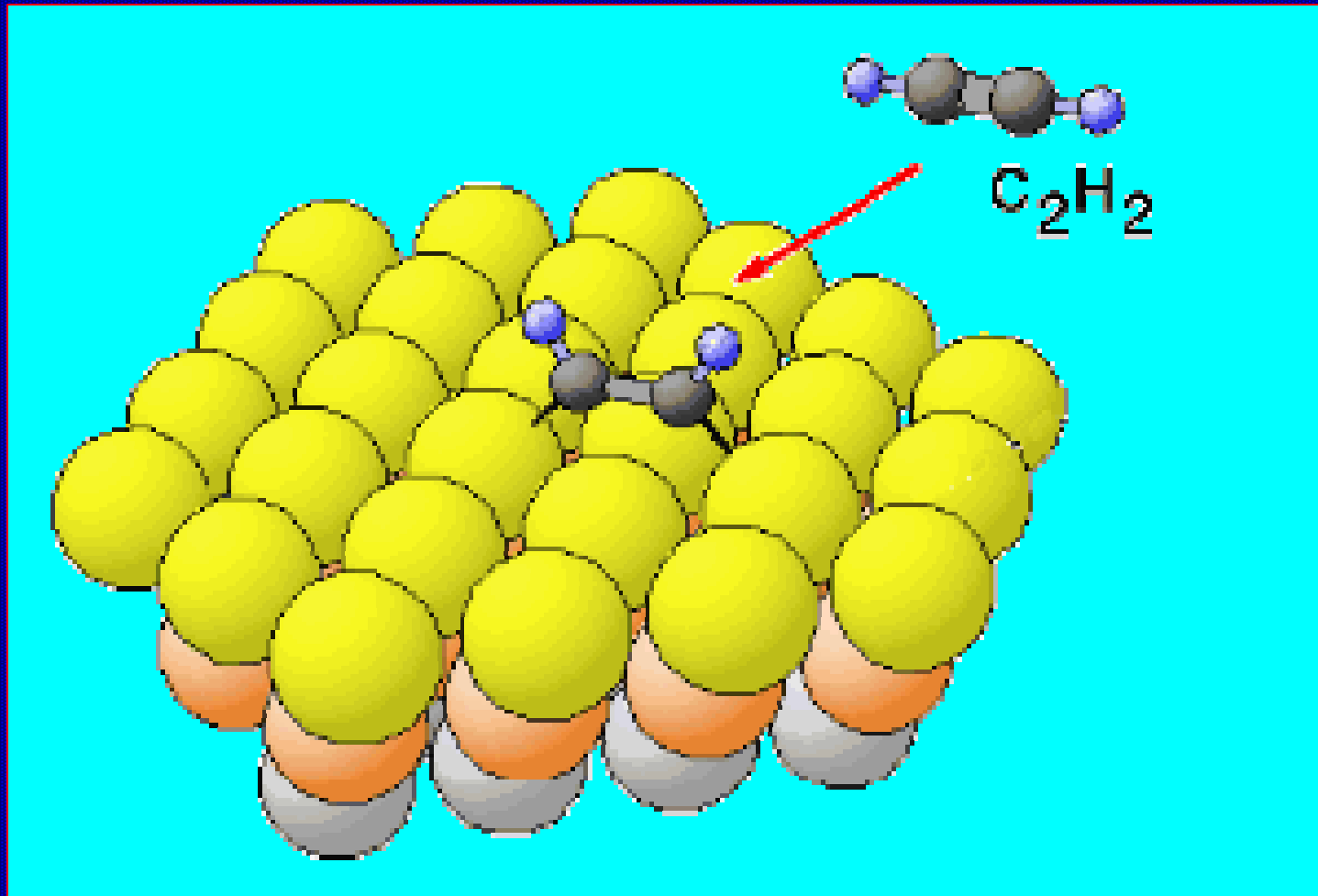


Initial physical adsorption is a most important feature of chemisorption

Variation of adsorption extent with temperature at a given pressure



Initial physical adsorption is a most important feature of chemisorption



Example of adsorption at solid gas interface
Cu(111) surface with an adsorbed acetylene molecule

Measurement of gas adsorption

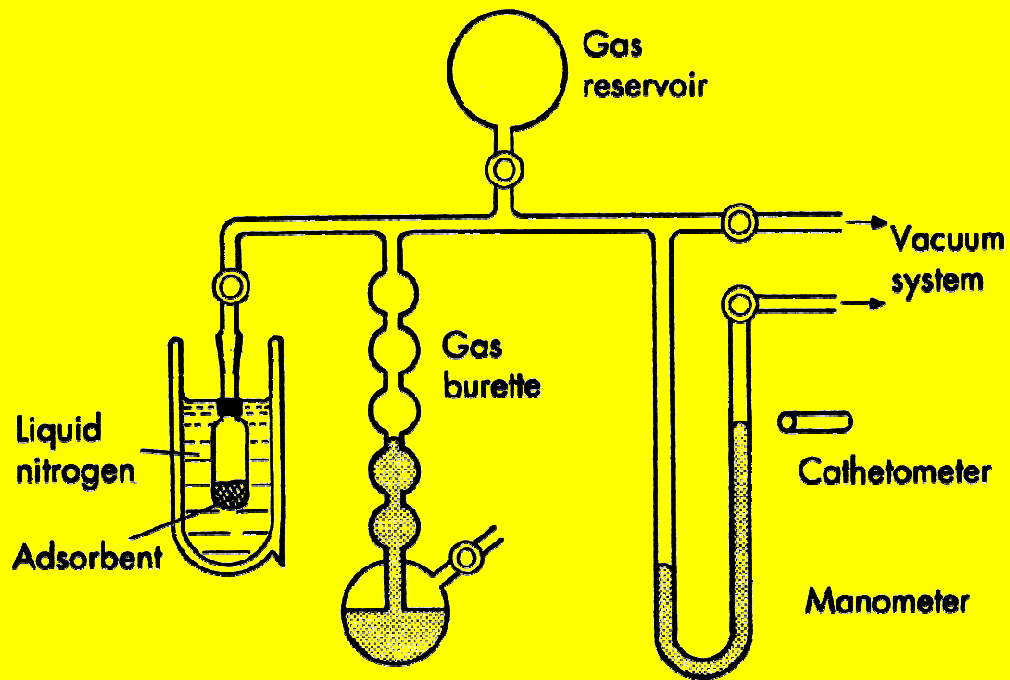


Figure 5.4 Volumetric apparatus for measuring gas adsorption at 77 K

Classification of Adsorption Isotherms

- *Three phenomena may be involved in physical adsorption*
 1. **Monolayer adsorption.**
 2. **Multi-molecular adsorption.**
 3. **Condensation in pores or capillaries.**

Normally, there is overlapping of these phenomena and interpretation of adsorption isotherms can be complicated.

IUPAC (Brunauer's) Classification

Type I,
Type II,
Type III,
Type IV,
and Type V
of isotherms

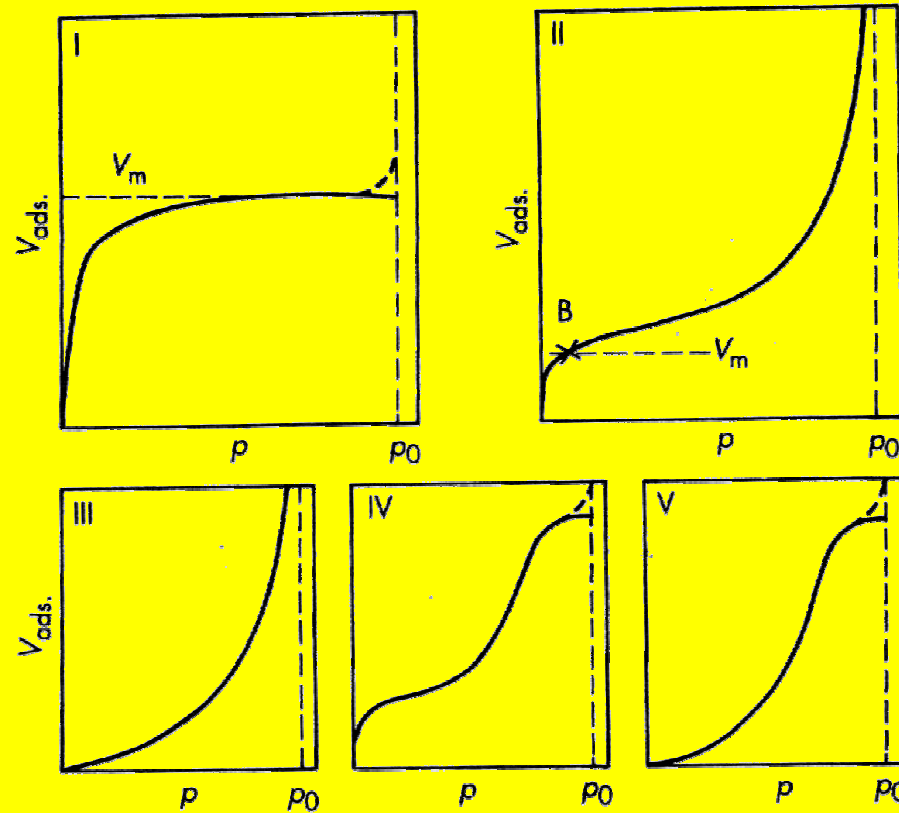


Figure 5.5 Brunauer's classification of adsorption isotherms (p_0 = saturated vapour pressure)

Capillary condensation

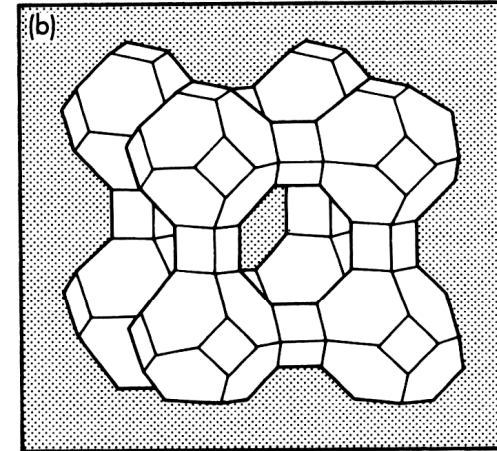
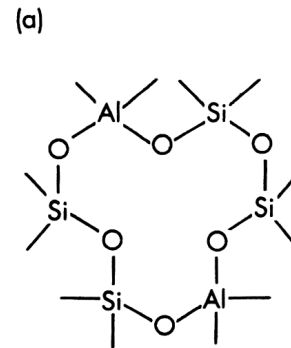
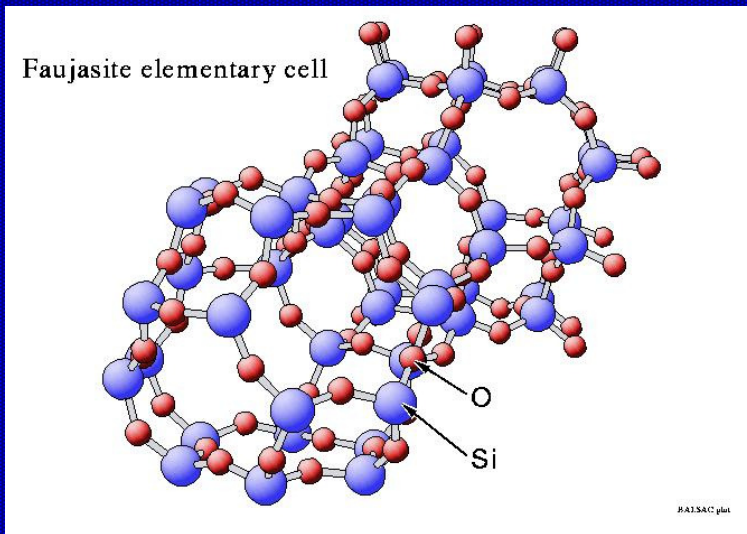


Figure 5.7 Zeolite structure. (a) 6-ring containing two aluminium and four silicon tetrahedral centres. (b) Zeolite A structure. Each of the eight sodalite units depicted contains 24 aluminium or silicon tetrahedral centres arranged to give six 4-rings plus eight 6-rings

Pores are usually classified according to their width as:

Micropores < 2 nm

Mesopores 2 – 50 nm

Macropores > 50 nm

Capillary condensation (Kelvin Equation)

Given that the vapour pressure over a convex liquid surface is greater than that over the corresponding flat surface.

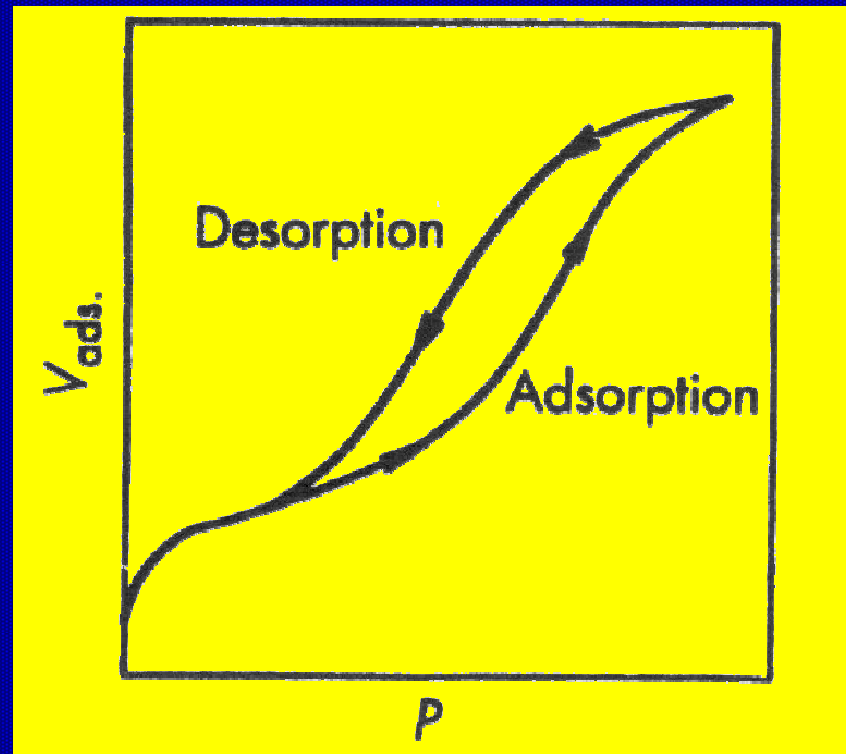
A liquid which wets the capillary form concave liquid – Vapour interface.

Therefore, the liquid has a lower vapour pressure in the capillary than it would have over a flat surface.

This vapour pressure difference is given by the Kelvin equation, in the form

$$RT \ln \frac{P_r}{P_o} = \frac{2\gamma V_m \cos \theta}{r}$$

Capillary condensation (Kelvin Equation)



Hysteresis Loop in physical adsorption

Isotherm Equations

- The Langmuir adsorption Isotherm

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{aV_m}$$

- The Freundlich adsorption
- The BET equation

$$\frac{P}{V(p_o - p)} = \frac{1}{V_m c} + \frac{(c-1) P}{V_m c P_o}$$

Surface area Calculation

- From The BET equation

$$V_m = \frac{1}{\text{slope} + \text{intercept}}$$