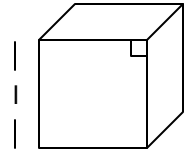


Ideal Surfaces

- Investigate how surface area varies with surface structure $area = 6 \cdot l^2$



- Particle size affect on surface area for cube.
- Let $l = 1 \text{ m}$; then total surface area = 6 m^2 .
- Cut cube into smaller cubes each having $l = 1 \times 10^{-6} \text{ m}$.
- There would be 10^{18} cubes in our cube with a side having a length of 1 m .
- Each cube has surface area of $area = 6 \cdot (1 \times 10^{-6} \text{ m})^2$
 $= 6 \times 10^{-12} \text{ m}^2$
- Total surface area would then be $total \text{ area} = 10^{18} \cdot 6 \times 10^{-12} \text{ m}^2$
 $= 6 \times 10^6 \text{ m}^2$
- \therefore For a fixed volume, surface area increases dramatically with smaller particle size – increasing 10^6 fold in this example.
- Often expressed as surface – to – volume ratio (S/V). In our example the volume is 1 m^3 so that the $S/V = 6 \text{ m}^{-1}$; for the smaller cubes,

$$S/V = 6 \times 10^6 \text{ m}^2 / 1 \text{ m}^3$$

$$= 6 \times 10^6 \text{ m}^{-1}$$

- Therefore, S/V ratio should be as high as possible to have an efficient use of the surface material.
- Dispersion also used to define the number of surface atoms:

$$D = \frac{\# \text{ surface atoms}}{\text{total number atoms}}$$

$$= \frac{n^3 - (n-2)^3}{n^3}$$

Ideal Surfaces: particle shape

- Compare the area of a cube with length of side, l , to the area of a sphere of radius, r ;

- For the same amount of the substance: $V_{\text{cube}} = V_{\text{sphere}}$

$$l^3 = \frac{4}{3} \pi r^3$$

$$l = \left(\frac{4}{3} \pi \right)^{1/3} r$$

- The ratio of the surface areas is: $\frac{S_{\text{cube}}}{S_{\text{sphere}}} = \frac{6l^2}{4\pi r^2}$ but $l = \left(\frac{4}{3} \pi \right)^{1/3} \cdot r$

$$\begin{aligned} &= \frac{6 \cdot \left(\frac{4}{3} \pi \right)^{2/3} \cdot r^2}{4\pi r^2} \\ &= 1.24 \end{aligned}$$

- Thus for the same amount of material, the surface area of the cubic structure will always be 1.24 times greater than for spherical particles.

Specific Surface Area

- S_{sp} = surface area / gram of material. Used in Chemical industry to describe the total area available per gram of material. Might include
 - Catalyst
 - “Inactive” Substrate
- S/V optimized by spreading the active component on the inert substrate.
- E.g. Assume Ni particles are spherical in and vary in size; the total volume of the particles is

$$V = \frac{4}{3} \pi \sum_{i=1}^n r_i^3 N_i = \frac{M}{\rho}$$

and the surface area is $S = 4\pi \sum_{i=1}^n r_i^2 N_i$

and the surface to volume ratio is $\frac{S}{V} = \frac{S}{M/\rho} = \frac{S_{sp}}{\rho} = \frac{4\pi \sum_{i=1}^n r_i^2 N_i}{\frac{4}{3} \pi \sum_{i=1}^n r_i^3 N_i}$

where M = mass of Ni; ρ = density of Ni

- Assume all particles are spherically shaped and the same size, $r = 0.10 \mu\text{m}$

$$S_{sp} = \frac{3}{\rho \cdot r}$$

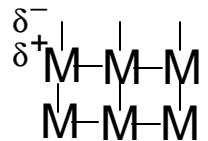
- Given: density = $3.0 \text{ g/cm}^3 = 3.0 \times 10^6 \text{ g/m}^3$.

$$S_{sp} = \frac{3}{3.0 \times 10^6 \text{ g/m}^3 \cdot 0.10 \times 10^{-6} \text{ m}} = 10.0 \text{ m}^2/\text{g}$$

- $r = 1.0 \mu\text{m}$: $S_{sp} = \frac{3}{3.0 \times 10^6 \text{ g/m}^3 \cdot 1.0 \times 10^{-6} \text{ m}} = 1.0 \text{ m}^2/\text{g}$

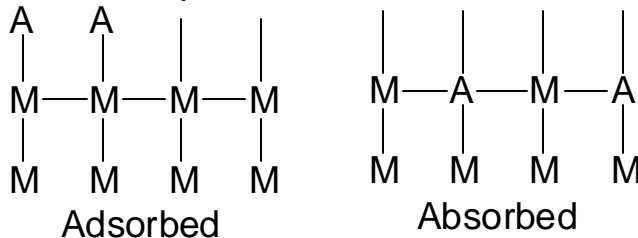
Real Surfaces

- Much more complicated \Rightarrow difficult to calculate the surface area with a simple equation such as just done.
 - Several shapes often co-exist.
 - Particles have irregular shapes such as pores (macroscopic) and other surface defects (microscopic).
- Microscopic scale: **steps**, **terraces** and **kinks** can be found on most surfaces.
- Co-ordination number is different for each site (kinks < steps < terraces); gives different reactivities.
- Atoms with smallest coordination number tend to be most reactive, since other atoms will tend to bond with them to give them the same coordination number as the rest.
- Dipoles exist because unbonded electron density extends out into the vacuum.
- Substances with lowest coordination number tend to have largest dipole. Dipoles (kinks > steps > terraces).
- Surface preparation techniques are very important because they control the relative number of each type of site and thus reactivity.
- Macroscopic scale: structure of the material has large affect on S/V ratio; note: this ratio is inversely proportional to the particle size (see earlier discussion).
- Structure can be quite complicated.
- Compare Ni with $r = 1 \mu\text{m}$ $S_{\text{sp}} = 1 \text{ m}^2/\text{g}$; activated charcoal $S_{\text{sp}} 1000\text{m}^2/\text{g}$ due to extensive pore structure.



Preparation of a Clean Surface

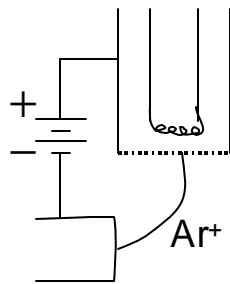
- Clean surface: a surface containing \leq a few atomic % of a single monolayer of “foreign atoms” – either adsorbed on or replacing surface atoms of a parent lattice.



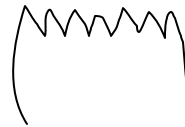
- Production and maintenance of a clean surface can only be accomplished with an ultra-high-vacuum (UHV) ($\approx 10^{-10}$ torr) since surface can be rapidly contaminated if the pressure is not in this range.
- Production of clean surfaces also requires the use of metals of the highest purity, since trace bulk components can migrate to the surface during the cleaning process. E.g. sample of 99.999% Ti contained large amounts of Cl, S from the bulk during the cleaning process.
- **High temperature Desorption:** applicable to single crystals, ribbons, and wires; crystallinity may be destroyed by the high T.
 - passing high current through wires attached to sample or send high energy electron beam at sample (up to several hours). Extended heating often causes bulk trace impurities to migrate to the surface (Cl, S, Si, C, O and some metals).
 - Chemically (occasionally) treat (O_2 or H_2) to remove adherent impurities.
 - Rapid heat to high temperature (close to T_{vap}) for few seconds in UHV. Removes impurities introduced during the first heating step where pressure can be quite high.
 - After initial cleaning steps, clean surface is obtained by flashing to high temperature. Applicable to many high melting metals (E.g. W, Mo, Re, Ru, Pt, Ni, etc.)

Clean Surfaces: Preparation

- **Inert gas ion bombardment:** Applicable to any solid; heating filament to ≈ 2500 K *in vacuo* causes
 - thermoionic emission of electrons;
 - Collision of electrons with inert gas such as Ar (at pressure of 10^{-7} to 10^{-5} torr depending upon system design; ionization of gas occurs.
 - Potential applied between the filament and an extracting grid accelerates the ions to the correct KE and directs them to the sample.
 - Ions can be moved around with deflection plates.



Sputtering Gun

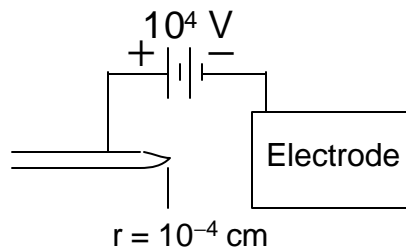


Sputtered Surface

- Bombarding roughens the surface, but induced roughness can be eliminated by annealing *in vacuo*. Embedded Ar will also be removed.
- Gases on the chamber walls desorb when inert gas atoms adsorb onto the walls; these molecules adsorb onto the surface. Problem can be reduced using a differentially pumped ion gun.
- Sample may need to be flashed to high temperature to eliminate any gases which are on the surface after sputtering.

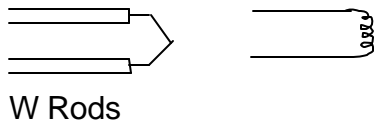
Clean Surfaces: Preparation 3

- **Field Desorption:** Applicable to field emission tips only. A potential of 10^4 V applied between sample and an electrode. Because of the small radius, field intensities of 10^8 Vcm⁻¹ develop at the sample tip. Atoms are stripped from the surface leaving a new layer of atoms to make up the new surface.

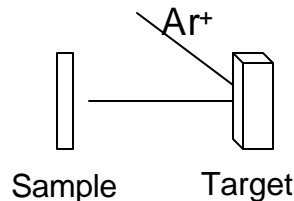


Field desorption

- **Vapor deposition of a film:** applicable to nearly any metal. Must have adequate volatility or be able to be heated to high enough temperature where vapor pressure is high enough.
 - Thermal deposition: metal heated to T by passing current through sample wire which is in intimate contact with the metal.
 - Vaporization assembly must be properly outgassed to insure that the system pressure is low during deposition ($\approx 10^{-8}$ Pa)



Vapor Deposition System



Sputter Deposition

- Sputter Deposition: Energetic ions sputter nonvolatile material from target to sample. Very common way of depositing material in the microelectronics industry.

Vapor deposition

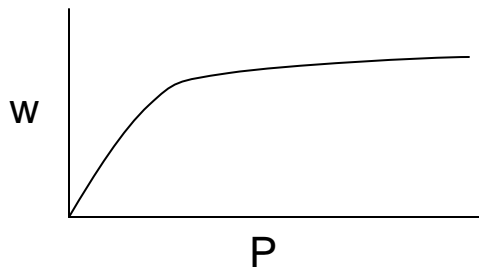
- Chemical vapor deposition (CVD): nonvolatile metals are often vapor deposited using volatile compounds of the metals.
 - Decomposed upon hitting the surface to produce the metal of interest.
 - Does not provide very clean surface, but deposits materials that might not otherwise be possible.
 - Commonly used in the microelectronic industry.
- Surfaces not uniform from any of these methods since surface structures tend to be columnar instead of crystalline.
- Crystals formed are small with high concentration of surface defects.
- Defects can be removed by heating to $T = (0.1-0.3) \cdot T_m$
- Upon heating to $T > 0.3 \cdot T_m$:
 - Diffusion in the solid is relatively rapid small crystals aggregate to larger structures.
 - Recrystallization occurs; forms low index planes of crystal, but still polycrystalline.
 - Mean grain size increases.
 - Mechanical strains (from misfit of the film on the substrate) relieved.
- Other methods:
 - *Chemical*: applicable to metal/inert oxide support; metals reduces with H_2 . Surface extremely suspect since small concentrations of impurities in the H_2 can cause large variations in the surface composition.
 - *Cleavage or crushing of single crystals* applicable to brittle metals or materials or become so when cooled to LN_2 temperatures. Surface is usually quite rough.

Evaporative vs single crystal

- Evaporative film:
 - most general method of producing a clean surface of many if not all metals.
 - Very clean surfaces can be produced.
 - Even after annealing surface is not structurally pure (i.e. more than one crystalline face present).
 - After annealing of the film adsorption properties are similar to those of a filament.
 - Tedious process since whole system must be thoroughly outgassed prior to deposition.
- Single Crystals:
 - Gives more structural information about the adsorptive properties of the surface.
 - Impurities can be large problem.
 - Preparation of a single crystal plus the cleaning can be extremely tedious – taking days or weeks to clean the surface of impurities as well as those that migrate to the surface during thermal cycling.

Gas Adsorption

- Most often used to determine the area of a real surface.
- Surface area often not able to be determined by any other technique on these surfaces, because of the complicated structure associated with a real surface (E.g. size and number of pores).
- Since gaseous substances can penetrate pores, they make it possible to determine the surface area of a material.
- Sample flooded with gas phase molecules so that a film forms on specific sites or perhaps non-selectively on all sites.
- At a low enough temperature, condensation of a gas on the surface occurs in a non – selective way. I.e. it adsorbs on all available sites.
- Let w = weight of gas adsorbed per unit weight of adsorbent. This $w = f(P, T, E)$ where E = interaction energy between gas molecule (adsorbate) and surface (adsorbent).
- Usually, experiments are done at constant temperature leaving $w = f(P, E)$.
- Pressure varied and the amount adsorbed measured producing an **adsorption isotherm**.
- E varies with adsorbate, adsorbent, and extent of adsorption leading to variations in the shape of the isotherm.



Adsorption Forces

- Adsorbate: Upon adsorption gas molecule becomes more ordered. $\Rightarrow \Delta S = \text{negative}$, because of loss of one of its translational degrees of freedom.
- Adsorbent: ΔS may change but not by much, since at most surface atoms may be reorganized.
- Overall: $\Delta S_{\text{total}} = \text{negative}$ and dominated by ΔS of adsorbate.
- Adsorption is spontaneous $\Rightarrow \Delta G = \text{negative}$.
- But $\Delta H = \Delta G + T \Delta S \Rightarrow \Delta H = \text{negative}$.
- These energies are the result of standard van der Waals forces:
 - *Ion – dipole* = ionic solid + polar adsorbate, e.g. adsorption of CO onto NaCl.
 - *Ion – induced dipole* = ionic solid + polarizable adsorbate, e.g. N₂ onto NaCl.
 - *Dipole – dipole* = polar solid + polar adsorbate, e.g. CO + metal oxide.
 - *Quadrupole – dipole interactions* = symmetrical molecules with different electronegativities, e.g. CO₂ has no dipole, but has a quadrupole and will interact with a metal oxide surface.
 - *London forces* = weaker forces than all of the above; result of induced dipoles resulting from random motion of electrons.

Physisorption vs Chemisorption

- These two forms of surface bonding are the generic modes of bonding that are the result of the above interactions.
- **Physisorption:** weak interaction of adsorbate with adsorbent. Bonding is usually the result of London forces interacting at the surface.
 - Bonding involves same forces that lead to liquification of vapors.
 - Compounds with high boiling point (have strong intermolecular interactions) adsorb more strongly than those with low boiling points.
 - The critical temperature (B.P.) is maximum temperature for significant physisorption.
- **Chemisorption:** strong intermolecular forces (discussed above) cause rearrangement of electrons between adsorbate and adsorbent.
 - Chemical bond forms between two;
 - More difficult to remove chemisorbed molecule than a physisorbed molecule from the surface.

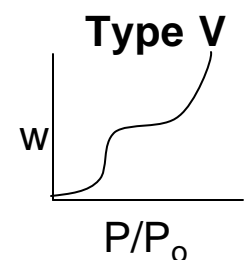
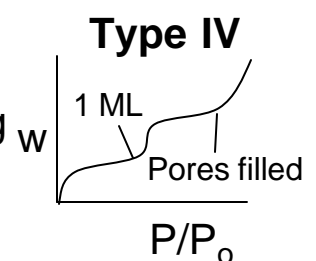
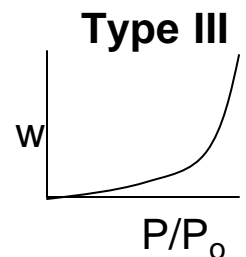
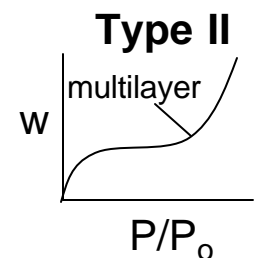
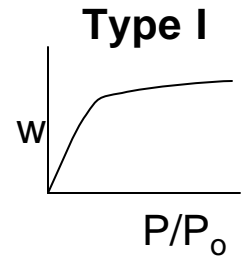
Distinguishing between Physisorption and Chemisorption

- Heat of adsorption: best criterion.
 - Physisorption: 8 – 25 kJ normal, but heats of adsorption as high as 80 kJ have been observed. These heats are roughly the same as the heat of liquification:
E.g. adsorption onto graphitized carbon black

	ΔH_{ads} , kJ/mol	ΔH_{liq} , kJ/mol
Ar	11.3	6.48
Kr	16.3	9.66
 - Chemisorption: Heat of adsorption is usually much higher (≥ 80 kJ/mol), e.g. O_2 adsorption on some metals ΔH_{ads} several hundred kJ/mol.
- Rate of adsorption:
 - Physisorption has no activation energy \Rightarrow very rapid adsorption with correct T.
 - Chemisorption: there is an activation energy of adsorption; not every adsorbate hitting the surface sticks to it. Rate of adsorption is generally lower than with physisorption.
- Rate of desorption:
 - E_a for desorption only a few kJ/mol for physisorption
 - E_a for desorption ≥ 80 kJ/mol for chemisorbed molecules and generally larger than ΔH_{ads}
- T_{ads} :
 - Minimum adsorption temperature is close to the boiling point of the adsorbate at the adsorption pressure. Porous materials where capillary forces are important will have $T_{\text{phys}} > T_{\text{bp}}$.
 - Min. adsorption temperature higher than boiling point of adsorbate.
- Specificity:
 - Physisorption is a form of condensation; little to no metal specificity (i.e. gas will adsorb on any metal).
 - Chemisorption: since heat of adsorption of an adsorbate is a function of the adsorbent, adsorbate is sometimes quite specific in terms of amount of adsorbate that will stick to a surface. E.g. $\approx 1/3$ monolayer of CO adsorbs on Ru, but little CO adsorbs on Ag.

Adsorption Isotherms

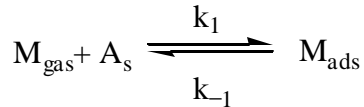
- 1940 Brunauer, Deming, Deming and Teller proposed that all adsorption could be described in terms of one of five isotherms.
- Type I: Only a few monolayers adsorb; asymptotically approaching limiting amount indicates that only surface sites adsorbed.
- Type II: Non – porous powders or at least powders with large pores produce isotherms of this shape. The large increase in the middle is associated with the build-up of multilayer structure.
- Type III: Observed when heat adsorption < heat liquification. As multilayer is approached, adsorption is facilitated.
- Type IV: similar to type II where adsorption is on porous material. 1st inflection due to formation of a monolayer and the second one due to the filling of the pores (pore radius 10 – 1000 Å).
- Type V same as Type III with pores.
- Measuring gas uptake is complicated because of the potentially complicated structures onto which we might wish to adsorb, but can understand some isotherms using Langmuir and BET theories.



Adsorption Isotherms: Langmuir

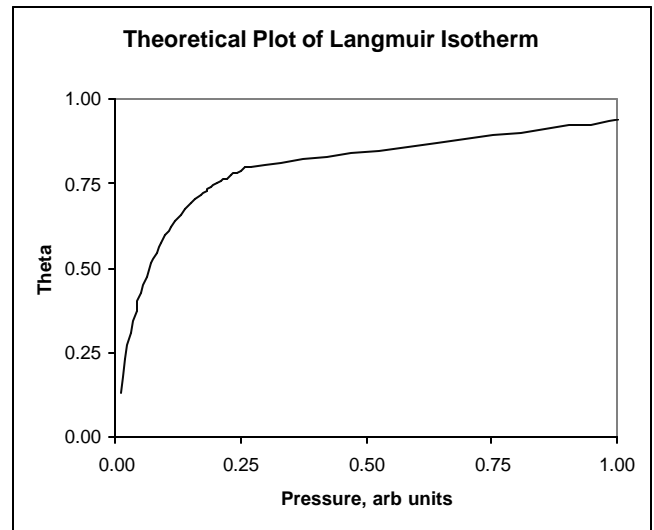
- Kinetic description of adsorption. Allows
 - Prediction of the number of adsorbate molecules to exactly cover the solid with a single molecular layer.
 - Calculation of the effective area covered by all of adsorbate molecules, where total area if monolayer (ML) = # molecules in one monolayer x effective area of the adsorbate molecule.
 - Applicable to Type I isotherm; assumes that adsorption is only a few monolayers at most of physisorbed adsorbate and of course 1 monolayer of Chemisorbed adsorbate.
 - Pores, which could be filled with larger amounts of adsorbate, are assumed to be insignificant.
- If we can tell from the isotherm when 1 ML has adsorbed, mass of adsorbate at that point will tell use the surface area.
- Chemisorption involves adsorption and forming of bonds between surface and adsorbate atoms. Measured surface area < than actual surface area.
- Assumptions:
 - Adsorbed species attached on surface at definite localized sites.
 - Each site has one and only one adsorbate.
 - Energy of each adsorbed species is the same at all surface sites and is independent of adsorbate – adsorbate interactions.

Langmuir Isotherm



- Model described by the reaction:
- Dynamic equilibrium assumed between gas phase and adsorbed molecules at a pressure developing some coverage θ = fraction of sites covered.
- Kinetic theory: # of molecules impinging on adsorbent surface per unit area in a unit time is $\propto P$.
- Rate of adsorption related to the fractional number of sites available.
 $R_{\text{ads}} \propto P(1 - \theta)$.
- Rate of desorption related to the coverage: $R_{\text{des}} \propto \theta$.
- Simplified derivation of Langmuir isotherm.
 - At steady state

$$\begin{aligned}
 R_{\text{ads}} &= R_{\text{des}} \\
 k_1 p(1 - q) &= k_{-1} q \\
 \frac{q}{1 - q} &= \frac{k_1}{k_{-1}} \cdot p = bp \\
 q &= bp(1 - q) \\
 &= bp - bpq \\
 q &= \frac{bp}{1 + bp}
 \end{aligned}$$



- This simplified model is in qualitative and quantitative agreement with observation for many adsorbates.

Langmuir Isotherm: Activation energy

- Velocity of Chemisorption depends upon: $M_{\text{gas}} + A_s \rightleftharpoons M_{\text{ads}}$
 - Pressure above the solution; since pressure determines the number of collisions per unit time and area.
 - Activation energy of chemisorption, E_a , since this determines the fraction of gas molecules with the necessary energy for Chemisorption.
 - Fractional coverage of the surface available for interaction with an adsorbate coverage of $f(\theta) = 1 - \theta$.
 - Steric of condensation factor, σ , fraction of total colliding molecules with the necessary activation energy, E_a , and orientation. Not the same as sticking probability, s , which is the total probability of a gas molecule sticking to the surface.
- Adsorption is then given by: $v_1 = s \cdot \frac{P}{(2\pi mkT)^{1/2}} \cdot f(\mathbf{q}) \cdot \exp(-E_a / RT)$

where

 - 2nd term is # molecules with mass, m , striking per unit area of surface in unit time.
 - Last term = fraction with the energy E_a .
- Desorption is likewise given by: $v_{-1} = k_{-1} \cdot \Phi(\mathbf{q}) \cdot \exp(-E_d / RT)$ where
 - k_{-1} = rate constant for desorption and is related to the vibrational frequency of the adsorbed molecule;
 - $\Phi(\theta)$ = fractional number of sites available for desorption. When only one adsorbate per site, $\Phi(\theta) = \theta$.
 - E_d = activation energy of desorption.

- Steady state

$$v_1 = v_{-1}$$

$$s \cdot \frac{P}{(2\pi mkT)^{1/2}} \cdot f(\mathbf{q}) \cdot \exp(-E_a / RT) = k_{-1} \cdot \Phi(\mathbf{q}) \cdot \exp\left(\frac{-E_d}{RT}\right)$$

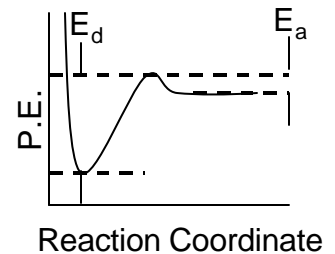
$$P = (2\pi mkT)^{1/2} \cdot \frac{k_{-1}}{s} \cdot \frac{\Phi(\mathbf{q})}{f(\mathbf{q})} \cdot \exp\left(\frac{-E_d + E_a}{RT}\right)$$

$$= (2\pi mkT)^{1/2} \cdot \frac{k_{-1}}{s} \cdot \frac{\Phi(\mathbf{q})}{f(\mathbf{q})} \cdot \exp\left(\frac{-Q}{RT}\right)$$

where $Q = E_d - E_a =$ heat of adsorption

Langmuir Isotherm: Activation energy2

- Lennard-Jones curve for Cu-H₂ demonstrates energy terms.
- Adsorbate must overcome an activation energy barrier, E_a, for it to chemisorb.
- Upon chemisorption, it gives up a heat, Q, where Q = E_d - E_a relative to the initial state.



- Desorption cannot occur until it acquires an energy equal to the desorption activation energy, E_d.

- Coverage terms, Φ(θ) and f(θ):

$$P = (2pmkT)^{1/2} \cdot \frac{k_{-1}}{s} \cdot \exp\left(\frac{-Q}{RT}\right) \cdot \frac{q}{1-q}$$

- One adsorbate – one site: Φ(θ) = θ; f(θ) = 1 - θ.
- One adsorbate – several sites: for every molecule adsorbing, several sites become available.
 - E.g. 100 plane of BCC metal such as alkali metal on W. One adsorbed atom blocks adsorption on the four nearest neighbor sites.
 - E.g. 2 Closest pack layer, the number of adsorbed molecules is 1/2 the number of surface sites.
- When one adsorbate occupies one site, the equation becomes:

$$P = (2pmkT)^{1/2} \cdot \frac{k_{-1}}{s} \cdot \exp\left(\frac{-Q}{RT}\right) \cdot \frac{q}{1-q}$$

- This is the same as the Langmuir equation derived earlier, when

$$\frac{1}{b} = (2pmkT)^{1/2} \cdot \frac{k_{-1}}{s} \cdot \exp\left(\frac{-Q}{RT}\right) \quad Q.E.D.$$

Using the Langmuir Equation

- Relative coverage: it is more convenient to express coverage in terms of the relative volume, V and V_m (= maximum volume adsorbed), adsorbed by the surface.

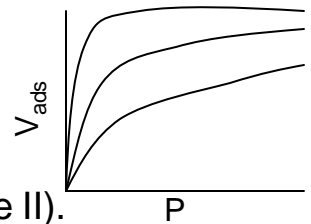
$$q = \frac{V}{V_m}$$

- Substitute into the Langmuir equation to get:

$$q = \frac{V}{V_m} = \frac{bp}{1+bp}$$

$$V = \frac{V_m bp}{1+bp}$$

- At very low P : $bP \ll 1$. The equation simplifies to $V = V_m bP$ or the amount adsorbed is linearly proportional to P . Recall first part of the isotherm.
- At high P : $V \rightarrow V_m$ asymptotically.
- Large Q : adsorbate is strongly adsorbed (top curve, Type I).
- Small $Q \Rightarrow$ weak adsorption (bottom curve, Type II).
- Variable Q as temperature increases, b increases, which causes a gradual change from Type I to Type II.

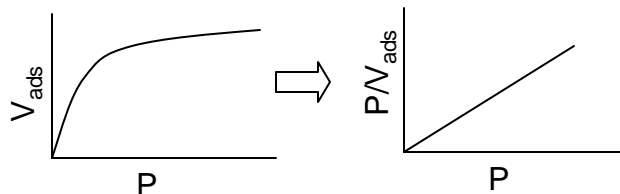


- Plotting data according to the Langmuir equation: $V = \frac{V_m bp}{1+bp} \Rightarrow \frac{1}{V} = \frac{1+bp}{V_m bp}$
linear behavior predicted when P/V vs P plotted.

E.g. Kr/ C at -183°C .

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m} \quad Q.E.D.$$

Linearity of plot indicated agreement with theory. Slope of graph should lead to V_m .



Langmuir Model, cont.

- Calculation of surface Area: $V \propto n \propto W \Rightarrow V_m \propto W_m$ and

$$\frac{V}{V_m} = \frac{W}{W_m} \quad \text{but} \quad \frac{V}{V_m} = \frac{bP}{1+bP} \quad \text{and} \quad \frac{P}{W} = \frac{1}{bW_m} + \frac{P}{W_m}$$

$$\frac{W}{W_m} = \frac{bP}{1+bP}$$

- Slope of the plot of P/W vs P gives W_m = the mass of adsorbate.
- Total surface area then determined using $s_T = N_m \cdot A$ where
 - N_m = number of molecules in a monolayer (from W_m) and
 - A is the cross-sectional area of an atom.
- Total surface area could also be calculated from: $s_T = W_m \cdot \frac{N_A}{MW} \cdot A$
- Failures with the model:
 - Does not account for the coverage dependent changes in Q , which are the result of lateral interactions between adsorbate molecules (atoms). Repulsion of like parts of the molecule.
 - Doesn't account for the other four isotherms, i.e. multilayer adsorption.
 - Cross-sectional area is often not known so that surface area cannot be determined even though the amount adsorbed is.

Slygin-Frumkin Isotherm

- Accounts for coverage dependent changes in heat of adsorption. Assumes:
 - Uniform surface, i.e. all sites are equivalent.
 - Linear decrease in Q with coverage.
 - 1 site adsorption (Langmuir isotherm)
- $Q = Q_0(1 - \alpha\theta)$ where α = proportionality constant; Q_0 = heat of adsorption when $\theta = 0$.
- Again recall: $bP = \frac{\theta}{1-\theta}$ and $b = \frac{\sigma}{k_{-1}(2\pi mkT)^{1/2}} \cdot \exp\left(\frac{Q}{RT}\right)$
 $= a_0 \cdot \exp\left(\frac{Q}{RT}\right)$
- Substitute for the coverage dependence of Q : $b = a_0 \cdot \exp\left(\frac{Q_0(1-\alpha\theta)}{RT}\right)$
- and $\frac{\theta}{1-\theta} = P \cdot a_0 \cdot \exp\left(\frac{Q_0(1-\alpha\theta)}{RT}\right)$
 $\ln\left(\frac{\theta}{1-\theta}\right) = \ln\left[P \cdot a_0 \cdot \exp\left(\frac{Q_0(1-\alpha\theta)}{RT}\right)\right] = \ln P + \ln A_0 - \frac{Q_0\alpha\theta}{RT}$
 $\ln P = \ln\left(\frac{\theta}{1-\theta}\right) - \ln A_0 + \frac{Q_0\alpha\theta}{RT}$
 where $A_0 = a_0 \cdot \exp(Q_0/RT)$
- For chemisorption $Q_0\alpha \gg RT$ since $RT \approx 2.5$ kJ/mol at 298 K; compared with $Q_{\text{chemi}} \geq 80$ kJ/mol.
- At medium coverage ($\theta \approx 0.5$), $\ln\frac{\theta}{1-\theta} \approx 0$ so that $\frac{Q_0\alpha\theta}{RT} \gg \ln\frac{\theta}{1-\theta}$
- Equation reduces to: $\ln P = -\ln A_0 + \frac{Q_0\alpha\theta}{RT} \vee \theta = \frac{RT}{Q_0\alpha} \cdot \ln(A_0 P)$
- Even though heat of adsorption varies with coverage in the low coverage range, coverage varies with P .

Brunauer-Emmett-Teller Isotherm

- Tempkin isotherm accounts for variations in Q , but still does not account for multilayer (Type II-V) formation on the surface.
- 1938 BET extended the Langmuir theory to multilayer adsorption.
- Assumptions:
 - Uppermost adsorbed molecular are in dynamic equilibrium with the vapor. I.e. the Langmuir equation applies to each portion of each layer that is exposed.
 - E_{ads} , E_{des} for first layer has a particular value; these values for the second and subsequent layers are the same, but not equal to first layer's.

- At equilibrium between the clean surface and 1 layer of adsorbed molecules: $V_1 = V_{-1}$

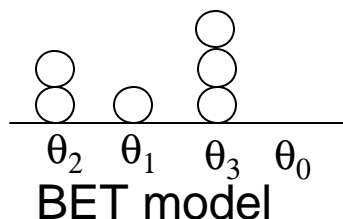
- Leads to
$$\frac{\sigma P}{(2\pi mkT)^{1/2}} \theta_0 \exp(-E_{a,0}/RT) = k_{-1} \theta_1 \exp(-E_{d,1}/RT)$$

$$a' \theta_0 P \exp(-E_{a,0}/RT) = k_{-1} \theta_1 \exp(-E_{d,1}/RT)$$

where
$$a' = \frac{\sigma P}{(2\pi mkT)^{1/2}}$$

- For every other layer: $a' \theta_{n-1} P \exp(-E_{a,n-1}/RT) = k_{-1} \theta_n \exp(-E_{d,n}/RT)$
- E_d , E_a are the same for all layers beyond the first one and should be equal to that of the liquid state.
- The equation for the other layers could then all be written as:

$$a' \theta_{n-1} P \exp(-E'_a / RT) = k_{-1} \theta_n \exp(-E'_d / RT)$$



BET model 2

- Rearrange these for the two sets of equations to get:

$$\frac{\theta_1}{\theta_0} = \frac{a \cdot P \cdot \exp\left(-\frac{E_{a,0} + E_{d,1}}{RT}\right)}{k_1} \quad \text{and} \quad \frac{\theta_n}{\theta_{n-1}} = \frac{a \cdot P \cdot \exp\left(-\frac{E'_a + E'_d}{RT}\right)}{k_1}$$

$$Q_a = E_{a,0} - E_{d,1} \quad \text{and} \quad Q_{\text{vap}} = E'_a - E'_d$$

- For each layer an equation can be written in terms of alpha and beta:

$$\theta_1 = \alpha \theta_0$$

$$\theta_2 = \beta \theta_1 = \alpha \beta \theta_0$$

$$\theta_3 = \beta \theta_2 = \alpha \beta^2 \theta_0$$

$$\theta_n = \beta \theta_{n-1} = \alpha \beta^{n-1} \theta_0$$

- Let $N_m = \#$ molecules adsorbed in a single layer, then the total # of molecules adsorbed at equilibrium will be:

$$N = N_m \cdot \theta_1 + 2 \cdot N_m \cdot \theta_2 + 3 \cdot N_m \cdot \theta_3 + \dots + n \cdot N_m \cdot \theta_n$$

$$= N_m \cdot [\theta_1 + 2 \cdot \theta_2 + 3 \cdot \theta_3 + \dots + n \cdot \theta_n]$$

- Use above to express all each part in terms of θ_0 .

$$\frac{N}{N_m} = a q_0 + 2 a b q_0 + 3 a b^2 q_0 + \dots + n a b^{n-1} q_0$$

$$= a q_0 [1 + 2 b + 3 b^2 + \dots + n b^{n-1}]$$

- But $(1 - b)^{-2} = [1 + 2 b + 3 b^2 + \dots + n b^{n-1}]$

- So that $\frac{N}{N_m} = a q_0 [1 - b]^{-2}$

- Next, we find an expression relating α and β by taking the ratio of the two:

$$\frac{a}{b} = \frac{\frac{a \cdot P \cdot \exp\left[(-E_{a,0} + E_{d,1}) / RT\right]}{k_{-1}}}{\frac{a \cdot P \cdot \left[\exp(-E'_a + E'_d) / RT\right]}{k_{-1}}} = \frac{\exp\left[(-E_{a,0} + E_{d,1}) / RT\right]}{\exp\left[(-E'_a + E'_d) / RT\right]}$$

$$= C = \text{const.}$$

$$a = b \cdot C$$

- Eliminate α to get: $\frac{N}{N_m} = C \cdot b \cdot q_0 [1 - b]^{-2}$

BET 3

- The sum of the fractional coverage must equal one:

$$\begin{aligned}
 1 &= \theta_0 + \theta_1 + \theta_2 + \dots + \theta_n \\
 &= \theta_0 + \alpha\theta_0 + \alpha\beta\theta_0 + \dots + \alpha\beta^{n-1}\theta_0 \\
 &= \theta_0[1 + C\beta + C\beta^2 + \dots + C\beta^n] \\
 &= \theta_0[1 + C\beta(1 + \beta + \dots + \beta^{n-1})]
 \end{aligned}$$

- Series in parentheses is an expansion of $(1 - \beta)^{-1}$, which gives:

$$1 = q \cdot \left[1 + \frac{bC}{1-b} \right]$$

- Divide into earlier relation:
$$\frac{N}{N_m} = \frac{bCq_0(1-b)^{-2}}{q_0 \cdot \left[1 + \frac{bC}{1-b} \right]} = \frac{bCq_0(1-b)^{-2}}{q_0 \cdot \left[\frac{1-b+bC}{1-b} \right]}$$
$$= \frac{bC}{(1-b)[1-b+bC]}$$

- Value of β vs P : $\beta \rightarrow 1$, when $P = P_0$.

$$b = \frac{a' \cdot P_0 \cdot \exp\left(-\frac{Q_{vap}}{RT}\right)}{k_{-1}} = 1$$

- Divide this into the original definition of β to get:

$$b = \frac{\frac{a' \cdot P \cdot \exp\left(-\frac{Q_{vap}}{RT}\right)}{k_{-1}}}{a' \cdot P_0 \cdot \exp\left(-\frac{Q_{vap}}{RT}\right)} = \frac{P}{P_0} \text{ substitute } \frac{N}{N_m} = \frac{\frac{P}{P_0} \cdot C}{\left(1 - \frac{P}{P_0}\right) \left[1 - \frac{P}{P_0} + \frac{P}{P_0} \cdot C\right]} = \frac{C}{\left(\frac{P}{P_0} - 1\right) \left[1 + (C-1) \cdot \frac{P}{P_0}\right]}$$

Mass and number of particles are proportional to each other so that we get:

$$\begin{aligned}
 \frac{w}{w_m} &= \frac{N}{N_m} = \frac{C}{\left(\frac{P}{P_0} - 1\right) \left[1 + (C-1) \cdot \frac{P}{P_0}\right]} \Rightarrow \frac{\left[1 + (C-1) \cdot \frac{P}{P_0}\right]}{C \cdot w_m} = \frac{1}{w \cdot \left(\frac{P}{P_0} - 1\right)} \Rightarrow \frac{1}{w \cdot \left(\frac{P}{P_0} - 1\right)} = \frac{1}{C \cdot w_m} + \frac{(C-1) \cdot \frac{P}{P_0}}{C \cdot w_m} \\
 \frac{1}{w \cdot \left(\frac{P}{P_0} - 1\right)} &= \frac{1}{C \cdot w_m} + \frac{1}{w_m} \cdot \frac{(C-1) \cdot \frac{P}{P_0}}{C} \quad Q.E.D.
 \end{aligned}$$

BET: Surface Area Determination

- Surface area will be determined by a plot of P/P_0 . Mass of monolayer, will provide a measure of surface area.
- Our equation predicts linear behavior, when we plot

$$\frac{1}{w(P_0/P - 1)} \text{ vs } \frac{P}{P_0}$$

- Valid only when $0.05 \leq \frac{P}{P_0} \leq 0.35$

- Slope, S, and intercept, I, will be

$$I = \frac{1}{w_m C} \wedge S = \frac{1}{w_m} \cdot \frac{C-1}{C} \Rightarrow C = \frac{1}{I \cdot w_m} \Rightarrow S = \frac{1}{w_m} \cdot \frac{1/(I \cdot w_m) - 1}{1/(I \cdot w_m)} = \frac{1}{w_m} - I$$

$$\boxed{w_m = \frac{1}{S+I} \wedge C = \frac{S}{I} + I}$$

- From w_m the total surface area is calculated: $S_T = N_m \cdot A$ where N_m = # of adsorbed particles and A the cross-section area of the adsorbing material.

- Leads to $\boxed{S_T = \frac{w_m}{MW} \cdot N_A \cdot A}$ where N_A = Avagadro's number.

- Adsorbate Cross-sectional Areas: Knowing the amount adsorbed and using one of the theories discussed, one should in principle be able to determine the total surface area, but need to know the cross-sectional area of the adsorbate.

- BET in 1937 assumed adsorbate spherical and used bulk properties to estimate the area.

– Area and volume would then be: $A = 4\pi r^2 \wedge V = \frac{4}{3}\pi r^3 \vee r = \left(\frac{3V}{4\pi}\right)^{1/3} \Rightarrow$

$$A = 4\pi \left(\frac{3V}{4\pi}\right)^{2/3}$$

- Volume is the volume of one molecule, which is determined from the molar volume and Avagadro's number.

$$\boxed{A = 4\pi \left(\frac{3V_{molar}}{4\pi N_A}\right)^{2/3}}$$

BET: Difficulties

- Lateral motion of adsorbate decreases ordering, which causes apparent surface area \leq true surface area. Adsorbate occupies more space when molecules are mobile.
- Complex molecules with rotational degrees of freedom around several axes can undergo conformational changes on various surfaces which would also cause variations in the cross-sectional area.
- Orientation of polar molecules produces different surface arrangements which depend upon the arrangement of the adsorbate.
- Localized adsorption as a result of strong chemisorption at specific sites means the cross-sectional area is proportional to the spacing between adsorption sites.
- Very small pores may not allow measurement of the area inside the pore, since adsorbate may not fit into pore.
- Ideal Adsorbates: $C \propto \exp(-Q_{\text{ads}}/RT)$
 - C should be small enough to assure no localized adsorption (localized adsorption gives low estimate S)
 - Small C gives lateral surface mobility \Rightarrow no organized structure; adsorbate behaves as a 2D gas.
 - Both low and high BET C values produce large errors; an intermediate value of C is thus ideal.
 - *Nitrogen* as a standard adsorbate:
 - C value of the intermediate size.
 - Small enough cross-sectional area for porous structures.
 - Accepted as the “standard” adsorbate with a cross-sectional area of 16.2 \AA^2 at -195.6°C (LN_2 temp.).

BET: Single Point Method

- BET method requires the measurement of several points to determine the shape of the adsorption curve. This takes lots of time.
- Single Point BET: Little loss of accuracy with the method.

- Recall S and I were defined as:

$$I = \frac{1}{w_m C} \wedge S = \frac{1}{w_m} \cdot \frac{C-1}{C}$$

- Their ratio is:

$$\frac{S}{I} = \frac{\frac{1}{w_m} \cdot \frac{C-1}{C}}{\frac{1}{w_m C}}$$

$$\frac{S}{I} = C - 1$$

- When $C \gg 1$, $I \ll S$. Our BET equation:

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

Becomes $\frac{1}{w \cdot \left(\frac{P}{P_0} - 1 \right)} = \frac{1}{w_m} \cdot \frac{(C-1)}{C} \cdot \frac{P}{P_0}$ since I is much smaller than S

$$\frac{1}{w \cdot \left(\frac{P}{P_0} - 1 \right)} = \frac{1}{w_m} \cdot \frac{(C-1)}{C} \cdot \frac{P}{P_0}$$

- Since $C \gg 1$, $C - 1 \gg C$ so that the equation becomes:

$$\frac{1}{w \cdot \left(\frac{P}{P_0} - 1 \right)} = \frac{1}{w_m} \cdot \frac{P}{P_0} \vee w_m = w \cdot \left(1 - \frac{P}{P_0} \right)$$

- Total Surface area is: $S_T = w_m \cdot \frac{N_A}{MW} \cdot A$

$$S_T = w \cdot \left(1 - \frac{P}{P_0} \right) \cdot \frac{N_A}{MW} \cdot A$$

- Measurement of surface area is then possible using amount adsorbed at some pressure as well as the other parameters.
- Routine surface area much more possible and single point method extensively used.

BET: Single- vs Multi-point

- To examine the relative error introduced by the single point method, we recall the equations for each:

- Multi-point $w_m = w \cdot \left[\frac{P_0}{P} - 1 \right] \cdot \left[\frac{1}{C} + \frac{(C-1)}{C} \cdot \frac{P}{P_0} \right]$

- Single-point $w_m = w \cdot \left(1 - \frac{P}{P_0} \right)$

- Relative error: $Rel.Error = \frac{w_{m,mp} - w_{m,sp}}{w_{m,mp}} = \frac{w \cdot \left[\frac{P_0}{P} - 1 \right] \cdot \left(\frac{1}{C} + \frac{C-1}{C} \cdot \frac{P}{P_0} \right) - w \left(1 - \frac{P}{P_0} \right)}{w \cdot \left(\frac{P_0}{P} - 1 \right) \cdot \left[\frac{1}{C} + \frac{C-1}{C} \cdot \frac{P}{P_0} \right]}$

$$Rel.Error = \frac{\left[\frac{P_0}{P} - 1 \right] \cdot \left(\frac{1}{C} + \frac{C-1}{C} \cdot \frac{P}{P_0} \right) - \left(1 - \frac{P}{P_0} \right) \cdot \frac{P_0}{P} \cdot \frac{P}{P_0}}{\frac{1}{C} \cdot \left(\frac{P_0}{P} - 1 \right) \cdot \left[1 + (C-1) \cdot \frac{P}{P_0} \right]} = \frac{\left[\frac{P_0}{P} - 1 \right] \cdot \left(\frac{1}{C} + \frac{C-1}{C} \cdot \frac{P}{P_0} \right) - \left(\frac{P_0}{P} - 1 \right) \cdot \frac{P}{P_0}}{\frac{1}{C} \cdot \left(\frac{P_0}{P} - 1 \right) \cdot \left[1 + (C-1) \cdot \frac{P}{P_0} \right]}$$

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

- Simplifying further:

$$Rel.Error = \frac{\left(1 - \frac{P}{P_0} \right)}{\left[1 + (C-1) \cdot \frac{P}{P_0} \right]}$$

Calculated Relative Errors

- Relative error evaluated for various values of P/P_0 and C :

C	P/P_0		
	0.1	0.2	0.3
1	0.90	0.80	0.70
50	0.17	0.07	0.04
1000	0.009	0.004	0.002

- Conclusions:
 - Relative errors reduced using higher pressures.
 - Increasing C minimizes error; When $C > 1$, single point method has an error of approximately 5-10%; remember we assumed $C \gg 1$.
- Although single point method should be used with the highest possible relative pressure, a relative pressure ≤ 0.3 can cause significant error in porous materials.