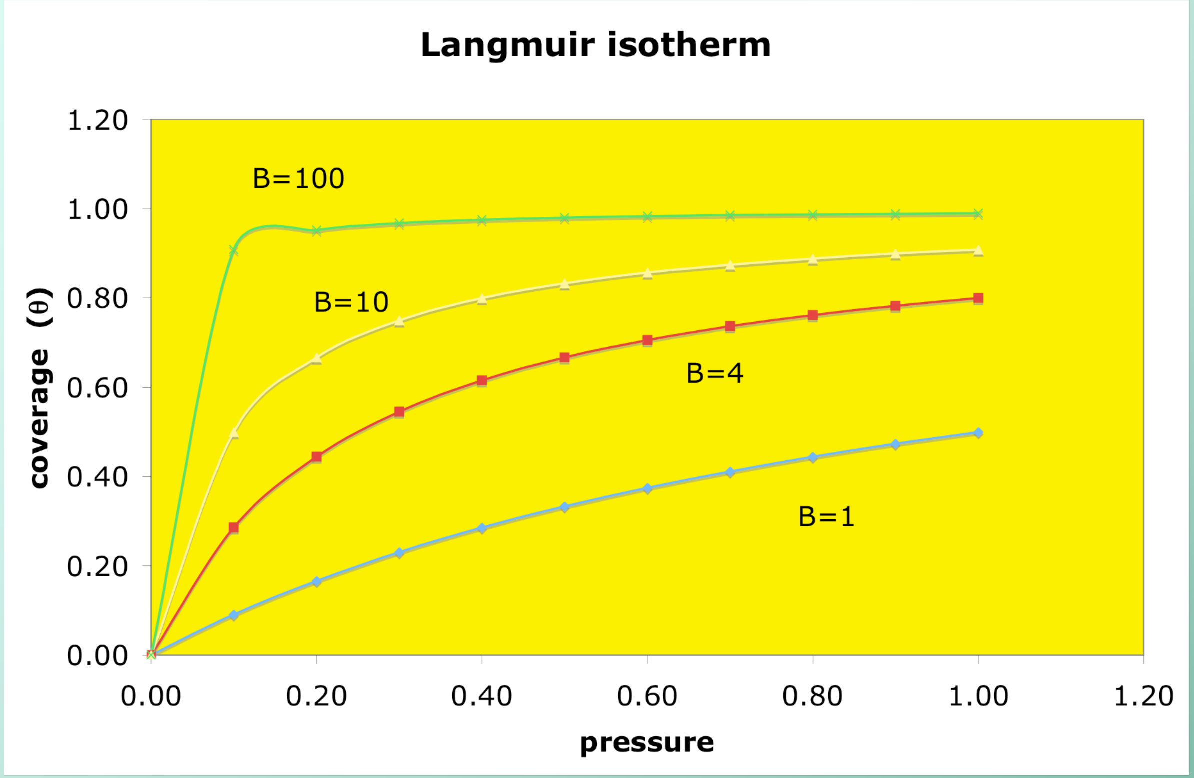


- Asymptotic limit at high p is θ=1, as reflected in assumptions.
- Interaction between solid and gas is represented by the constant B. θ rises with B at a given pressure.

$$B = {}^{1}\!\Big/_{kT}\left({q^{ads}}\Big/\left({q^{gas}}\big/_{V} \right) \right)\exp\left({\varepsilon_o^{gas} - \varepsilon_o^{ads}}\Big/_{kT} \right)$$

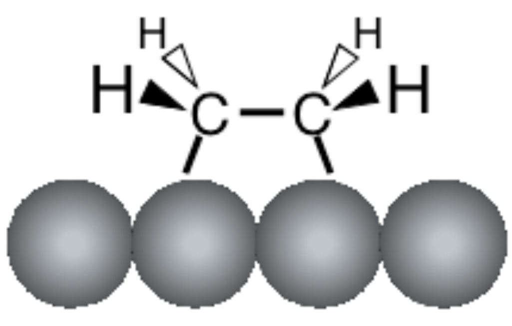
- Variation dominated by exponential i.e.
- ε^{gas} - ε^{ads} , the strength of the bond to the surface.
- *T*. B (and coverage) falls as *T* rises (exothermic process).

Typical numbers

- $q^{gas}/V = 2\text{x}10^{32}$ for 40 amu atom, 300K
- $q^{ads} = 1$ (rigid surface bond)
- $\varepsilon^{gas} - \varepsilon^{ads} = 50\ \text{kJmol}^{-1}$ (typical surface bond)
- yields $\theta = 0.5$ at P ~ 2000 Pa ~ 10^{-2} atm.
- *i.e.* adsorption very readily occurs!

Is the Langmuir isotherm successful?

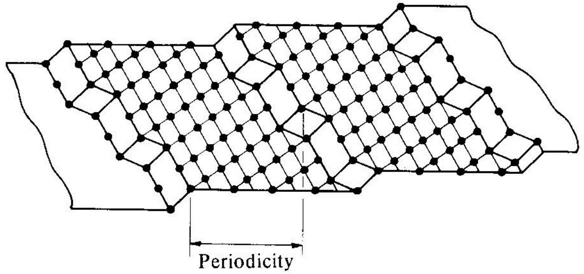
- Correct, at least qualitatively, for adsorption systems where the molecule chemically bonds to the surface. “chemisorption”
- In these systems, adsorption beyond a monolayer is impossible.



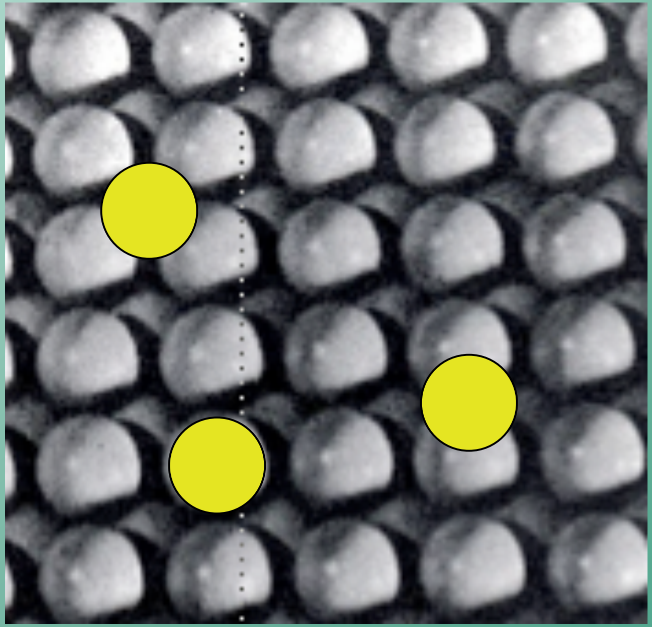
Quantitative failures in describing chemisorption systems

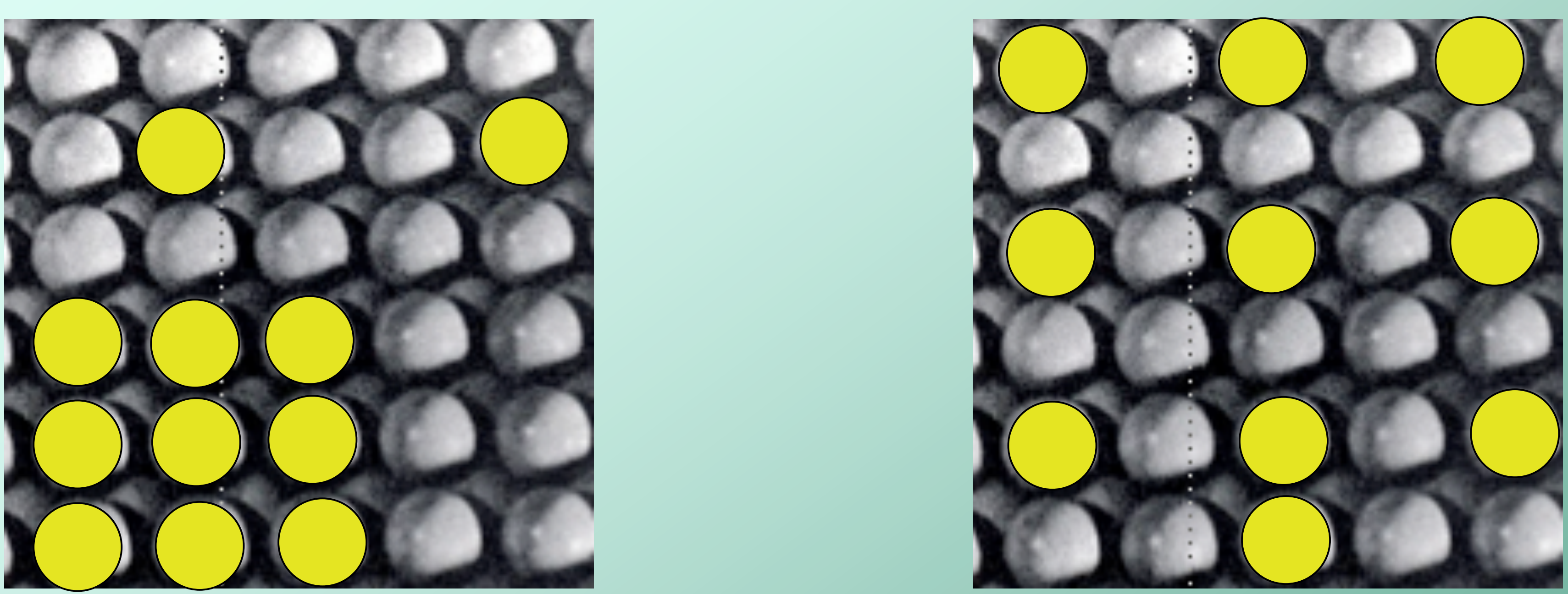
- Surfaces are’nt uniform
- So the heat of adsorption isnt constant.

Even a structurally uniform surface can have different sites



Kinked and stepped Pt (679) or Pt (S) [7 (111) × (310)]





- Adsorbed species can attract or repel each other.
- So adsorption can be ordered rather than random and again this causes variation in heat of adsorption

Any improvements?

- Various isotherms exist based on the “Langmuir” model but with heats of adsorption which vary with coverage in particular ways.
- Improve empirical representation of data, but yield little further insights into the surface chemistry involved.

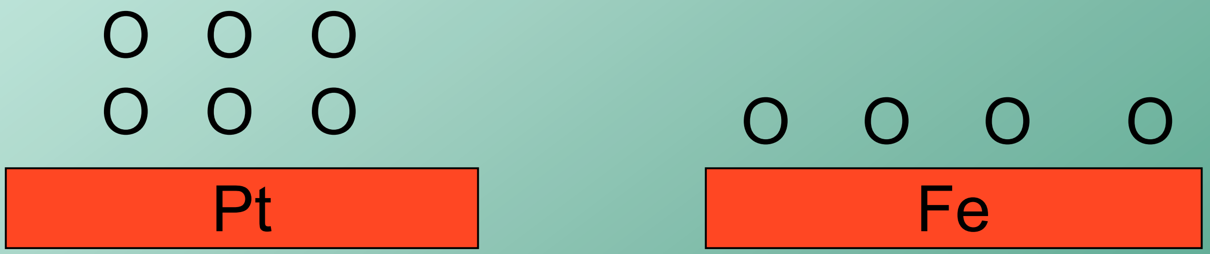
$$N^{ads} = \beta p^{1/\kappa} \qquad \theta = \beta \ln(\kappa p)$$

Freundlich

Temkin

Dissociative adsorption using Langmuir’s approach

- On many surfaces, molecules tend to dissociate spontaneously
- Need to modify the equations



A$_2$ (gas) → A$_2$ (ads)

$$\mu^{gas} = \mu^{ads}$$

$$X - kT\ln {}^{1}\!/_{p} = Y - kT\ln\left({}^{1}\!/_{\theta} - 1\right)$$

$${}^{1}\!/_{Bp} = {}^{1}\!/_{\theta} - 1$$

1/2 A$_2$ (gas) → A (ads)

$$\tfrac{1}{2}\mu^{gas} = \mu^{ads}$$

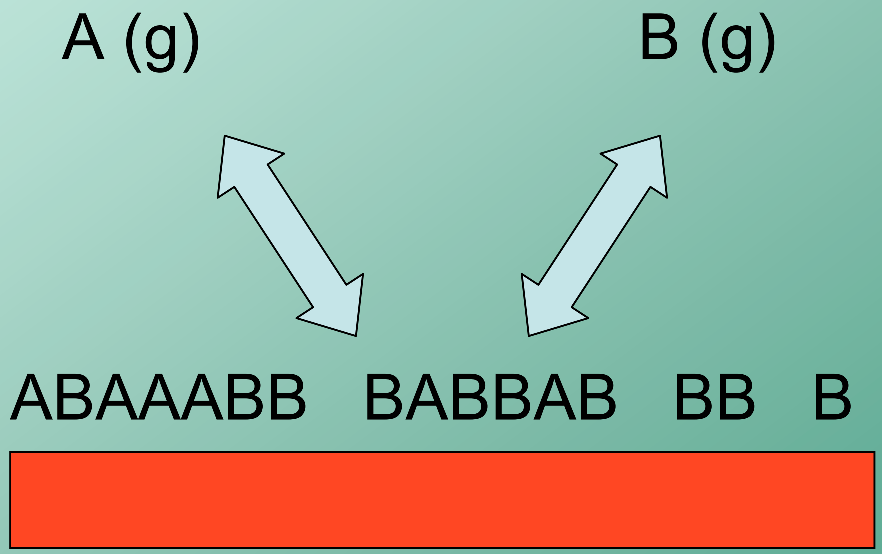
$$\tfrac{1}{2}\left(X - kT\ln {}^{1}\!/_{p}\right) = Y - kT\ln\left({}^{1}\!/_{\theta} - 1\right)$$

$${}^{1}\!/_{Bp^{\frac{1}{2}}} = {}^{1}\!/_{\theta} - 1$$

$$\theta = \frac{Bp^{1/2}}{1 + Bp^{1/2}}$$

Competitive adsorption

- Can have 2 or more gas phase species adsorbing on the same surface
- If one species is adsorbed, the other is blocked - “competitive adsorption”



A (g)

B (g)

ABAAABB BABBAB BB B

$$rate\ of\ ads. = rate\ of\ ads.$$

$$k_A^{ads}\left(1-\theta_A-\theta_B\right)p_A = k_A^{des}\theta_A$$

$$k_B^{ads}\left(1-\theta_A-\theta_B\right)p_B = k_B^{des}\theta_B$$

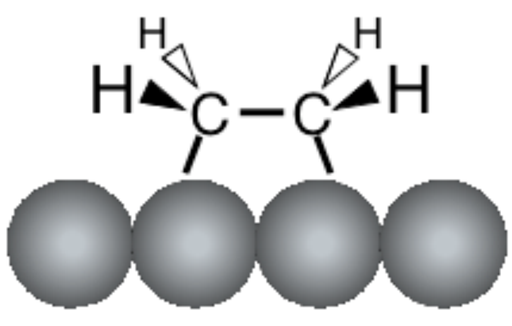
- Solve simultaneously for $\theta_{A,}\ \theta_B$

$$\theta_A = \frac{B_A P_A}{1+B_A P_A + B_B P_B} \qquad \theta_B = \frac{B_B P_B}{1+B_A P_A + B_B P_B}$$

$$\theta_A = \frac{B_A P_A}{1+\sum_i B_i P_i}$$

Physisorption

- Models and discussion above is relevant to chemisorption - chemical bond between adsorbate and surface.

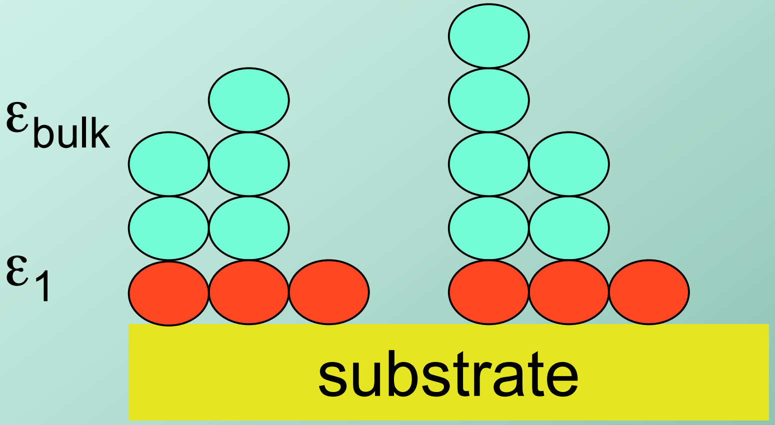


- But a second mode of adsorption exists "physisorption"
- Weak physical forces of interaction (dispersion, dipole etc.)
- ΔH_{ads} small (< 20 kJ mol^{-1})
- Related to condensation

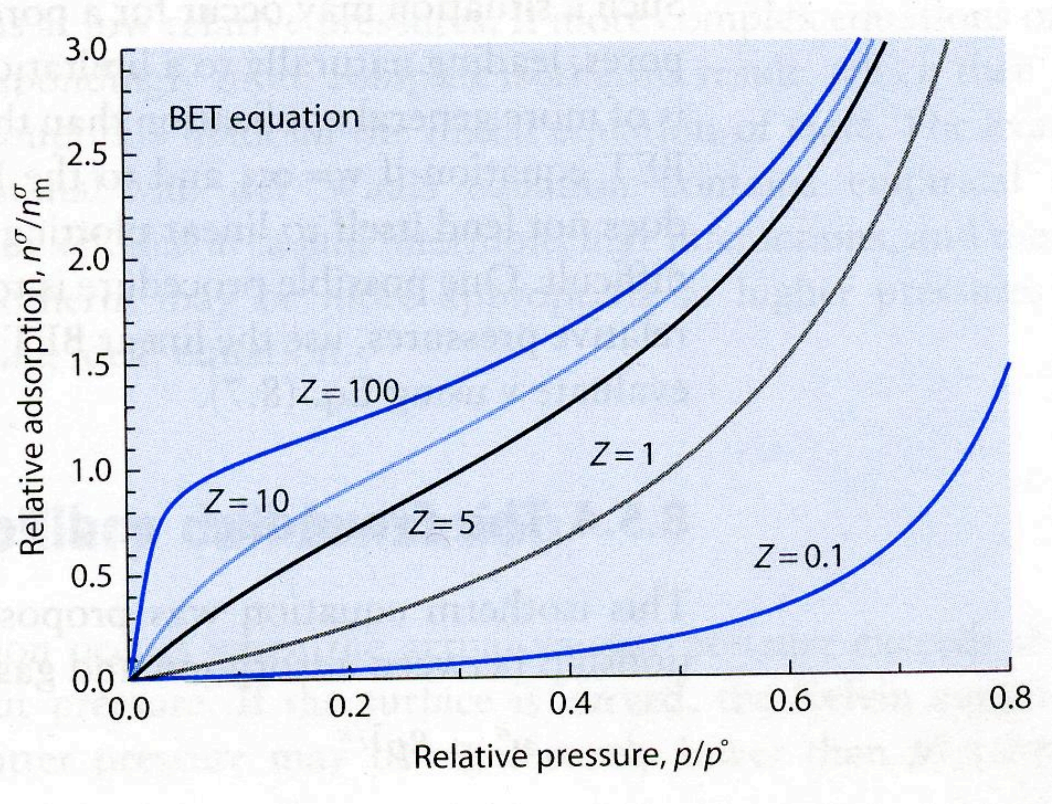
Some characteristics of physisorption

- Observed universally (e.g. inert gases) in contrast to chemisorption.
- But significant pressures required because of low ΔH_{ads}.
- Best described in terms of the *relative pressure* p/p_o where p_o is the saturated vapour pressure.
- At high relative pressures (p/p_o close to 1) observe multilayer formation.

- 🔴 Molecule in first layer (mainly molecule-substrate forces)
- 🔵 Molecule in multilayer phase (mainly molecule-molecule forces)



$$Z \approx \exp\left(\varepsilon^{bulk} - \varepsilon^{1} \middle/ kT\right)$$



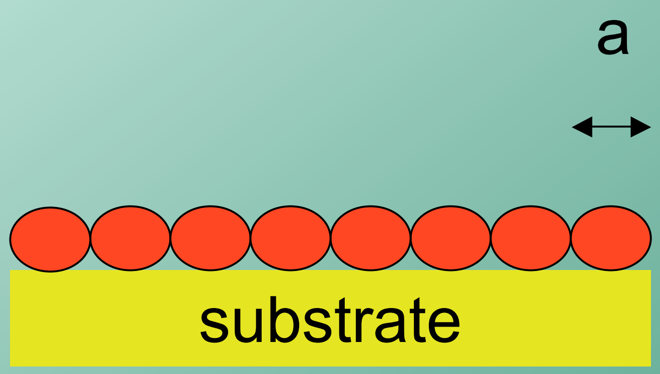
Some applications of the Langmuir isotherm

1. Measurement of the surface area of powders

e.g. pigments; absorbents (molecular sieves etc); phosphors; heterogeneous catalysts

- Often have internal and external "surfaces"

- how many molecules (N^{ads}) are adsorbed when the surface is saturated with a molecule of cross-section “a”?
- Surface area = $N^{ads} \times a$
- So we need a reliable way of determining the “monolayer capacity”



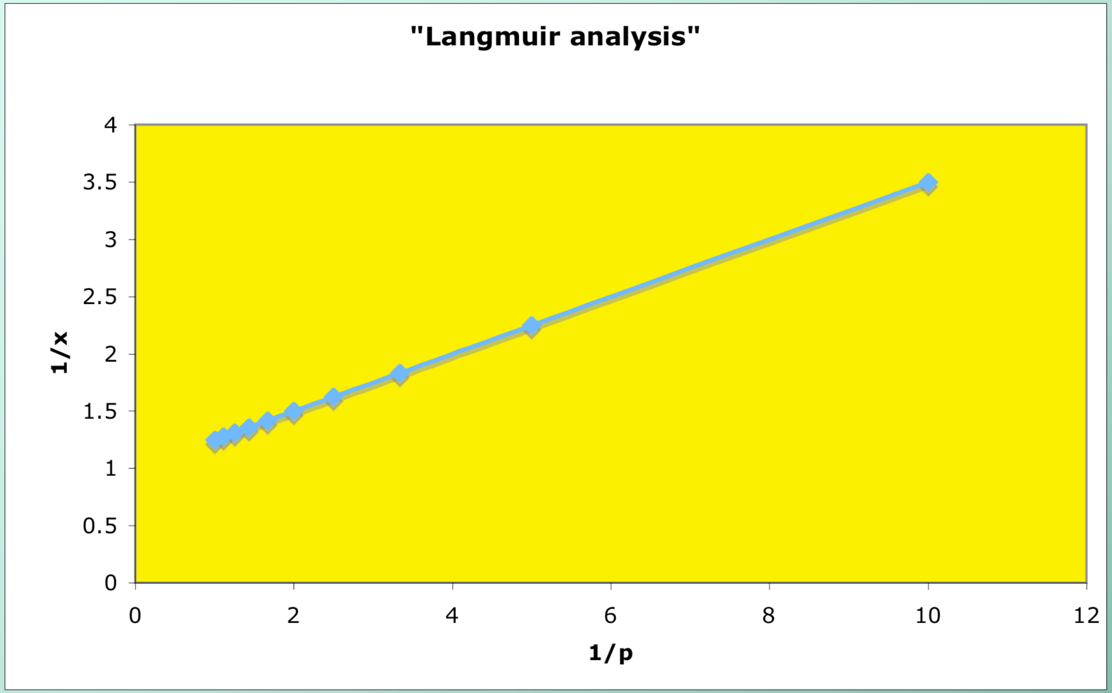
- Re-write θ as x/x^m where
    - x is mass of gas adsorbed
    - x^m is mass of gas adsorbed at saturation (the unknown, same units as x)
- So becomes

$$\theta_A = \frac{Bp_A}{1+Bp_A} \qquad {}^{x}\!/\!_{x^m} = \frac{Bp}{1+Bp}$$

which rearranges to

$$ {}^{1}\!/\!_{x} = {}^{1}\!/\!_{x^m Bp} + {}^{1}\!/\!_{x^m}$$

so measure x for differing p and plot 1/x vs1/p



According to above analysis, intercept = $1/x^m$ and Slope = $1/(x^m B)$ enabling both x^m and B to be determined.

- If a = area of adsorbed molecule
  M = molecular weight (same units as x)
  S = surface area (same units as a)

$$S = \left(x^m / M\right) \times \left(N_{avo}\right) \times \left(a\right)$$

Note: this Langmuirian approach works best for *chemisorption* - area is the “reactive” surface. “Total” area can be determined using *physisorption* and an applicable isotherm (BET eq.)