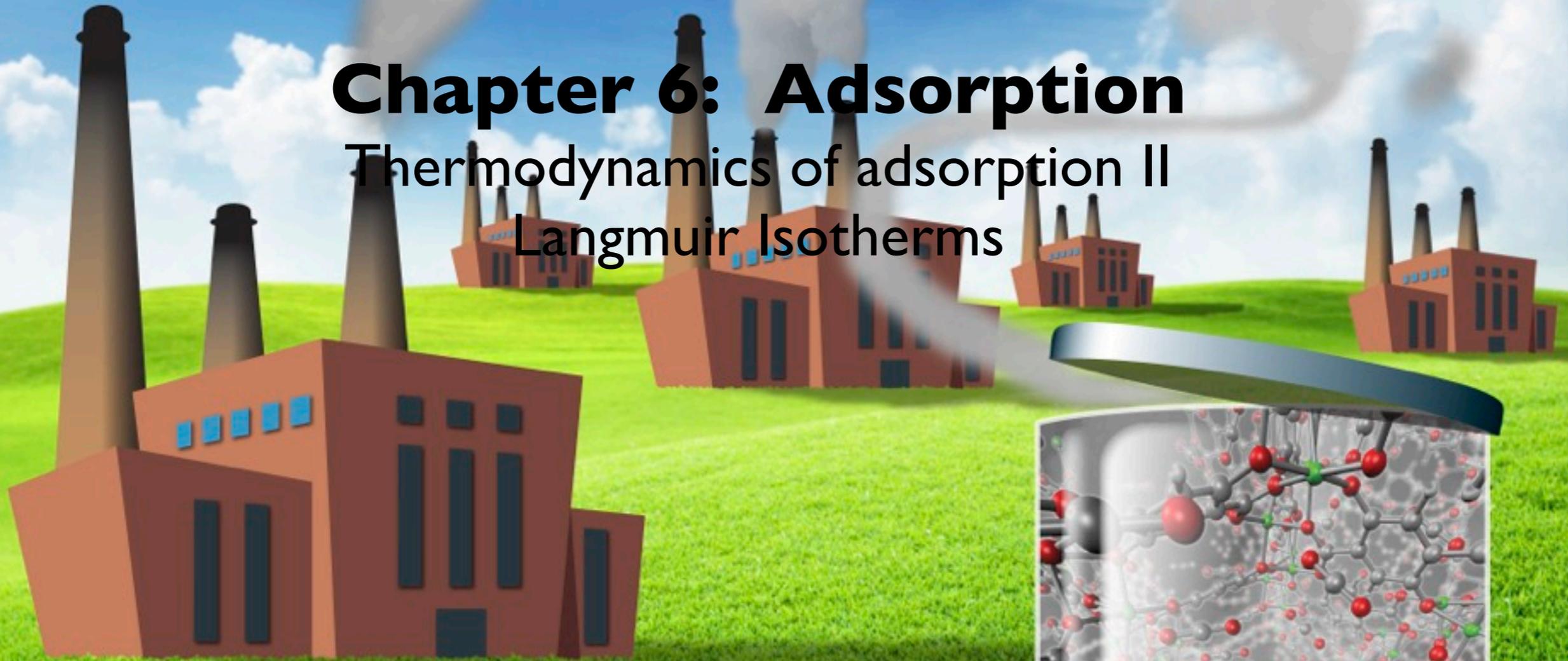


Introduction to Carbon Capture and Sequestration

Chapter 6: Adsorption

Thermodynamics of adsorption II
Langmuir Isotherms

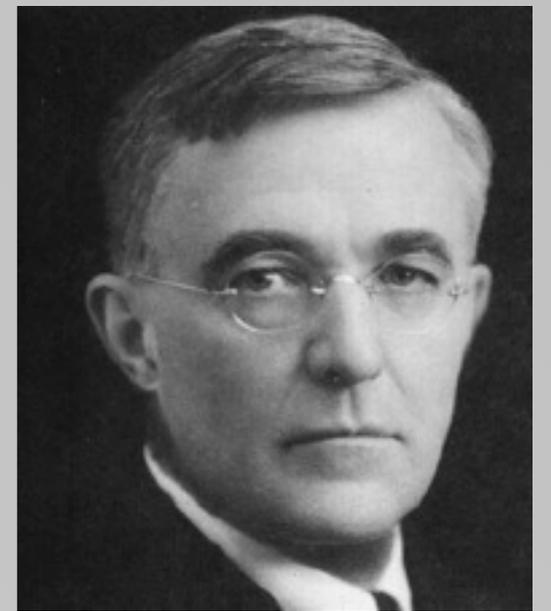


Chapter 6: Adsorption

Thermodynamics of Adsorption II (Langmuir Isotherms)

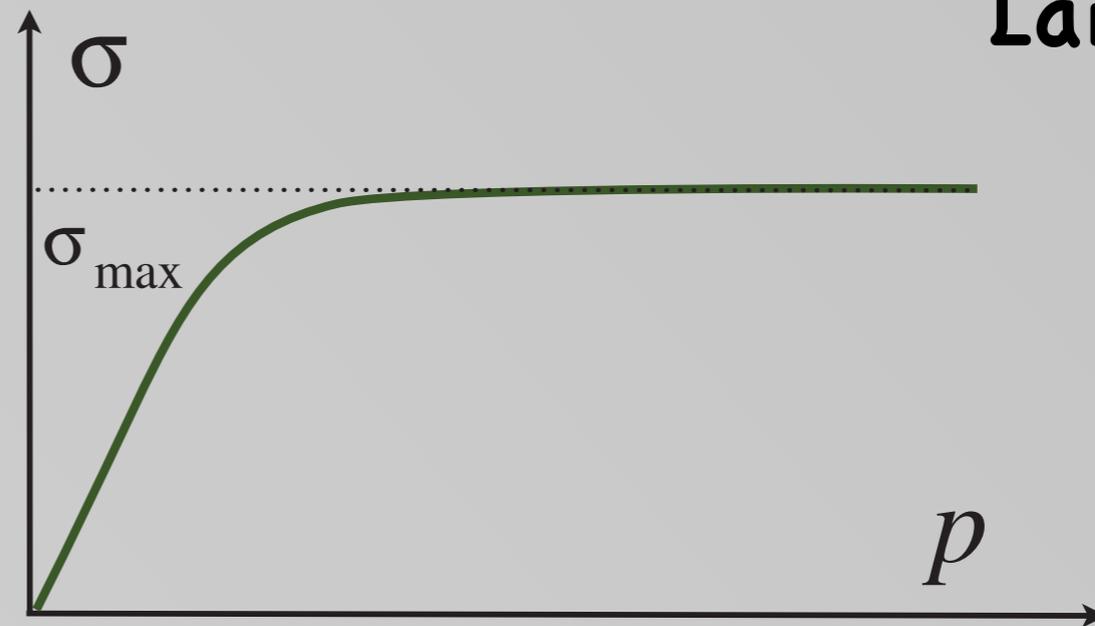
- Langmuir Isotherms
- Thermodynamic derivation of the coefficients

The simplest description of an adsorption isotherm is the **Langmuir adsorption isotherm**



Langmuir

$$\theta = \frac{\sigma}{\sigma_{\max}} = \frac{bp}{1 + bp}$$



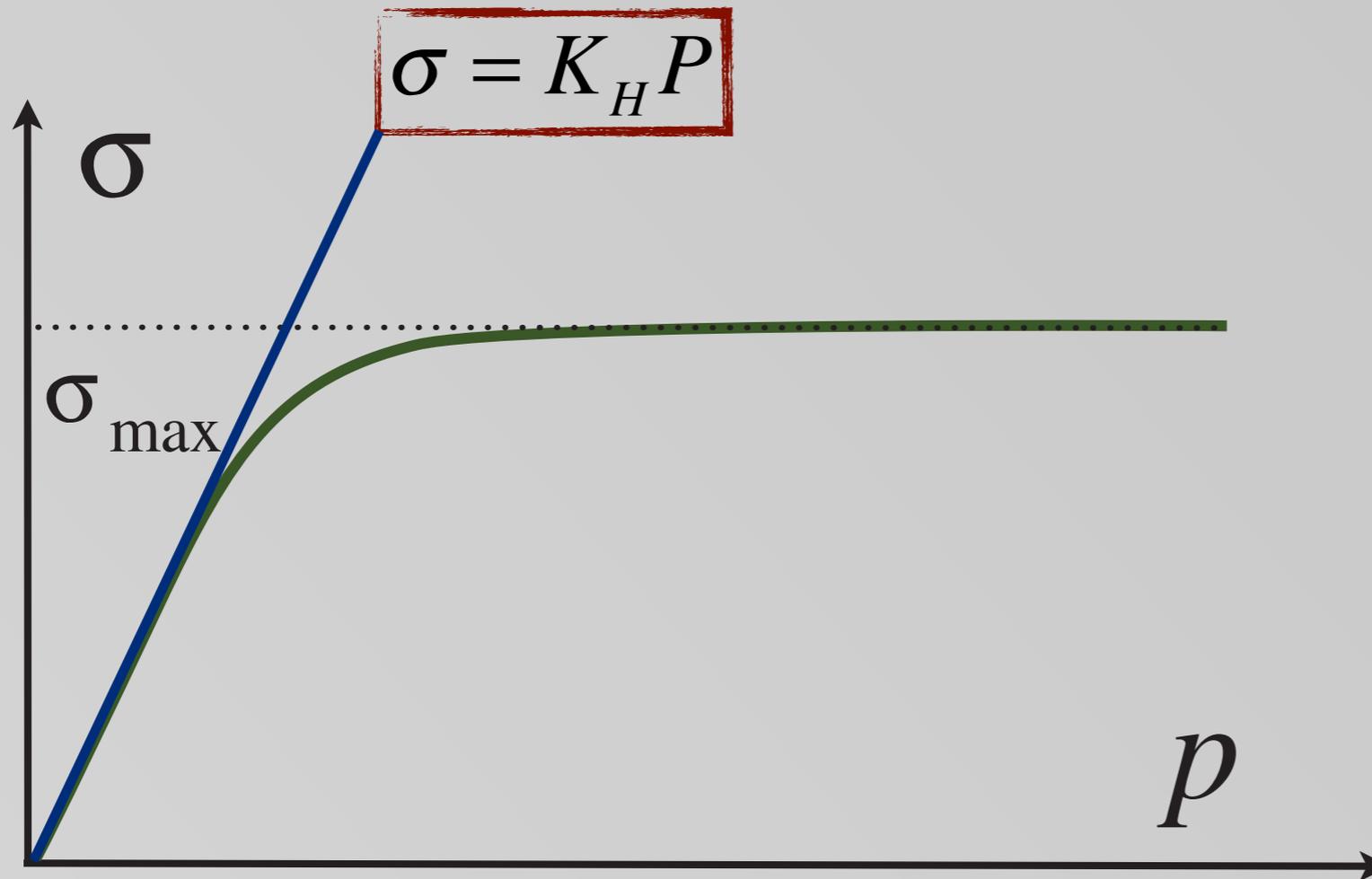
where θ is the fractional coverage and p is the bulk pressure

the Langmuir adsorption isotherm

Consider the limit $p \rightarrow 0$

Henry coefficient:

$$K_H = \lim_{p \rightarrow 0} \frac{\sigma}{p} = \lim_{p \rightarrow 0} \sigma_{\max} \frac{b}{1 + bp} = \sigma_{\max} b$$



Thermodynamics

Equilibrium of the CO₂ between
the gas and the adsorbed phase:

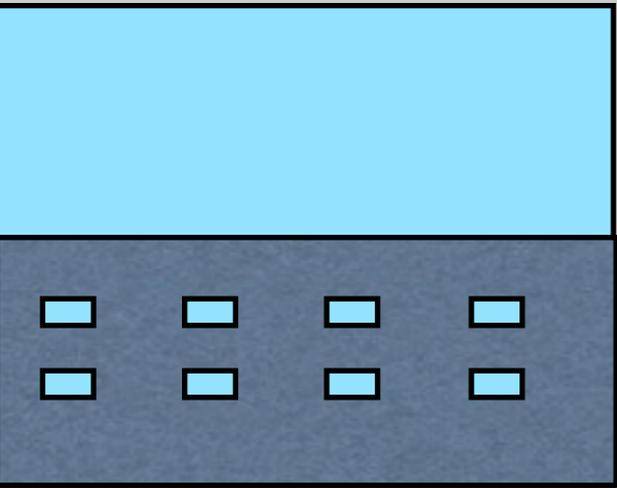
$$T^{gas} = T^{ads} = T$$

$$\mu_{CO_2}^{gas}(T, p) = \mu_{CO_2}^{ads}(T, \sigma)$$

(equal **chemical potential** and equal **temperature**)

We need an expression for the chemical
potential of a molecule in the gas phase
and in the adsorbed phase

Thermodynamics



Let us assume that the gas is an ideal gas:

Chemical potential of an ideal gas:

$$\mu^{IG}(T, \rho) = \mu^0(T) + k_B T \ln \rho$$

Boltzmann's constant

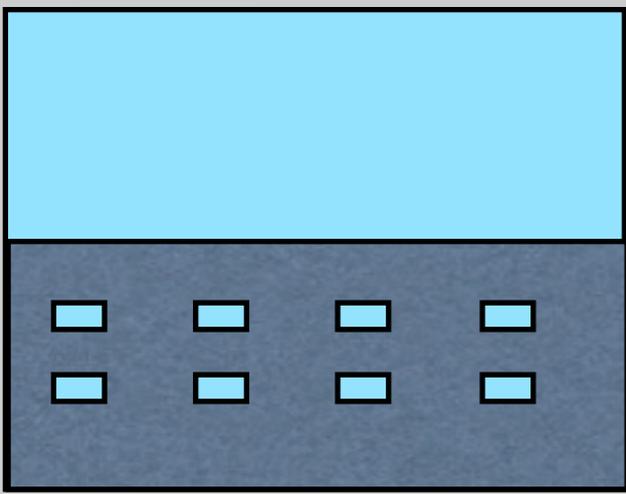
density

reference chemical potential

With the ideal gas law:

$$\mu^{IG}(T, p) = \mu^0(T) + k_B T \ln \frac{p}{k_B T}$$

Thermodynamics



loading: number of adsorbed molecules per unit volume

For the adsorbent:

ideal gas chemical potential

excess chemical potential

$$\mu^{ads}(T, \sigma) = \mu^{IG}(T, \sigma) + \mu^{ex}(T, \sigma)$$

If we use the expression for the ideal gas chemical potential:

$$\mu^{ads}(T, \sigma) = \mu^0(T) + k_B T \ln \sigma + \mu^{ex}(T, \sigma)$$

Thermodynamics

Equilibrium:

$$T^{gas} = T^{ads} = T$$

$$\mu_{CO_2}^{gas}(T, p) = \mu_{CO_2}^{ads}(T, \sigma)$$

Gas phase:

$$\mu^{IG}(T, p) = \mu^0(T) + k_B T \ln \frac{p}{k_B T}$$

For the absorbent:

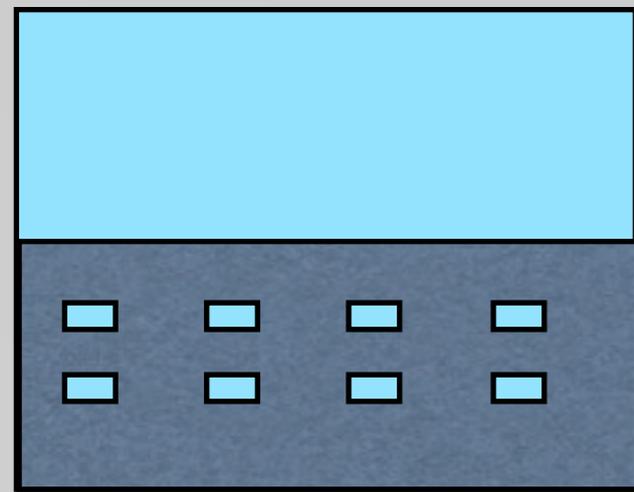
$$\mu^{ads}(T, \sigma) = \mu^0(T) + k_B T \ln \sigma + \mu^{ex}(T, \sigma)$$

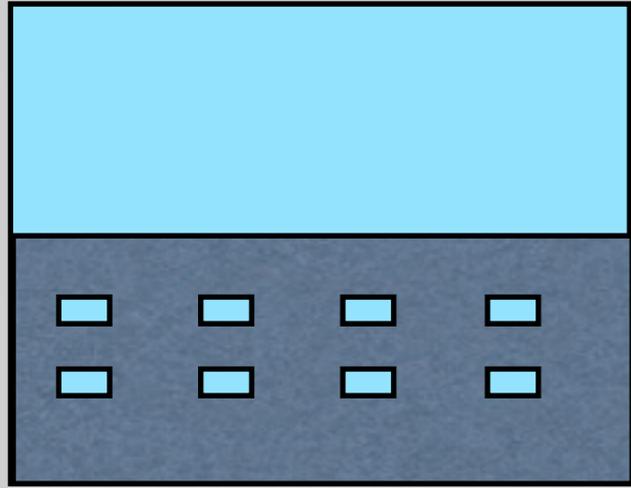
Equilibrium:

$$\ln \left(\frac{p}{k_B T} \right) = \ln \sigma + \frac{\mu^{ex}(T, \sigma)}{k_B T}$$

or

$$\sigma = \frac{p}{k_B T} \exp \left(- \frac{\mu^{ex}(T, \sigma)}{k_B T} \right)$$



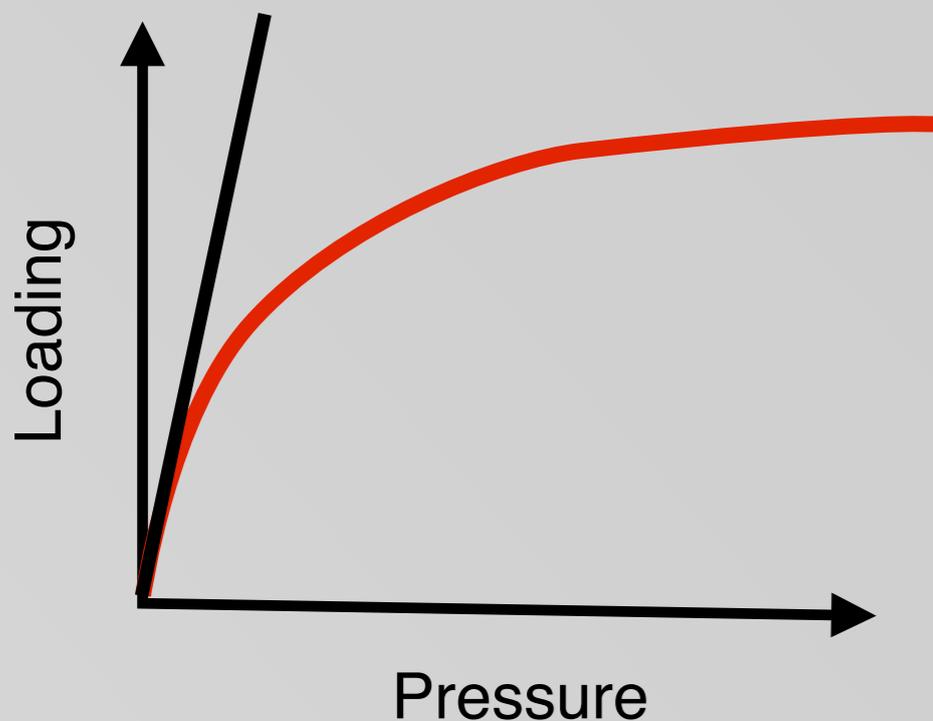


$$\sigma = \frac{p}{k_B T} \exp\left(-\frac{\mu^{ex}(T, \sigma)}{k_B T}\right)$$

Let us take the limit
 $p \rightarrow 0$, or $\sigma \rightarrow 0$

$$\sigma = \frac{p}{k_B T} \exp\left(-\frac{\mu^{ex}(T, 0)}{k_B T}\right) = K_H p$$

This defines the Henry coefficient K_H



$$K_H = \frac{1}{k_B T} \exp\left(-\frac{\mu^{ex}(T, 0)}{k_B T}\right)$$

At **low pressures** this gives a good approximation

Summary

The Henry coefficient, or Langmuir coefficient, is related to the excess chemical potential of a single molecule in the adsorbent.