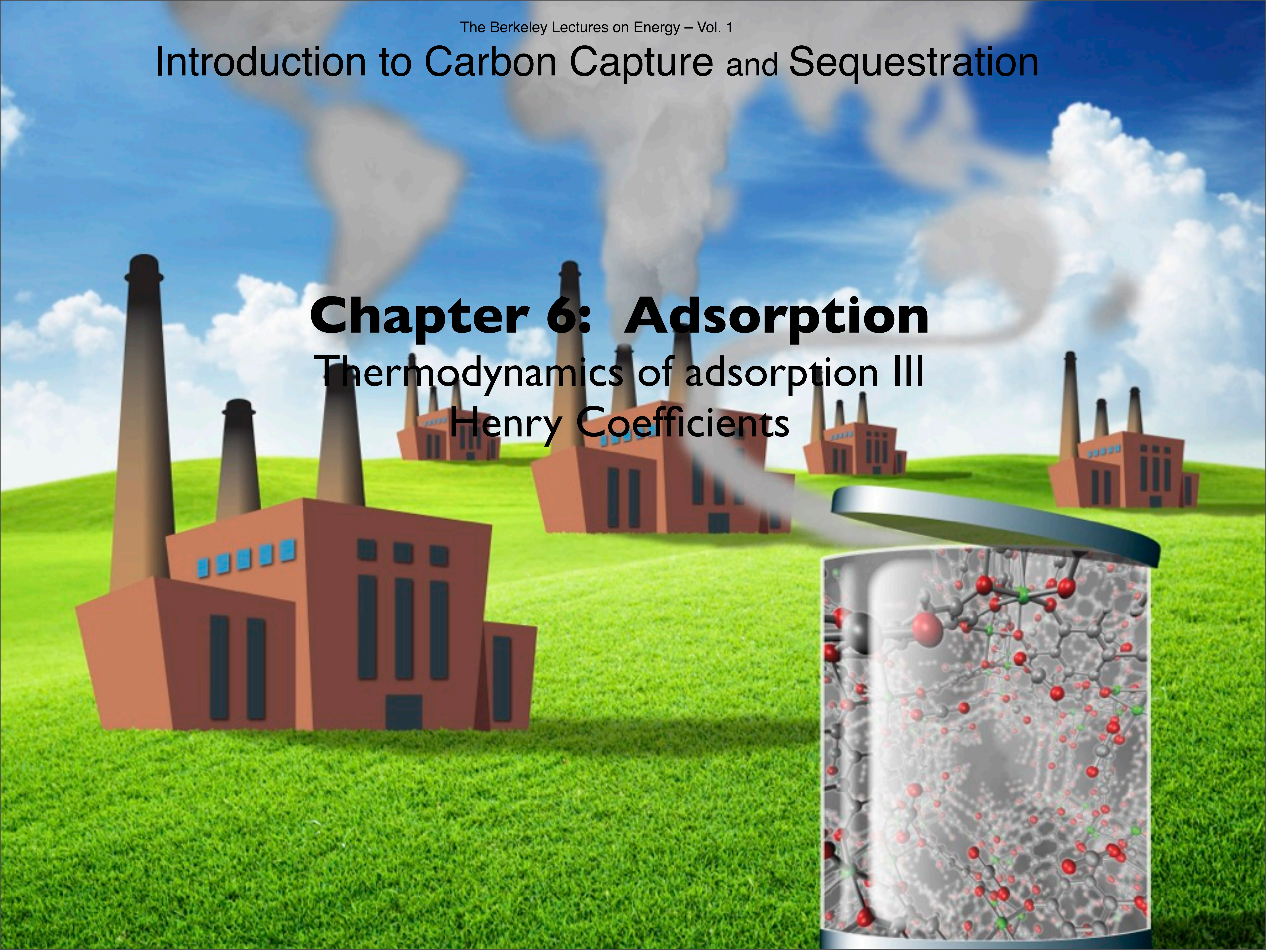
Introduction to Carbon Capture and Sequestration

Chapter 6: Adsorption

Thermodynamics of adsorption III
Henry Coefficients



Chapter 6: Adsorption
Thermodynamics of Adsorption III
(Henry Coefficients)

- Calculate the Henry coefficient of some model materials

Henry coefficient:

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

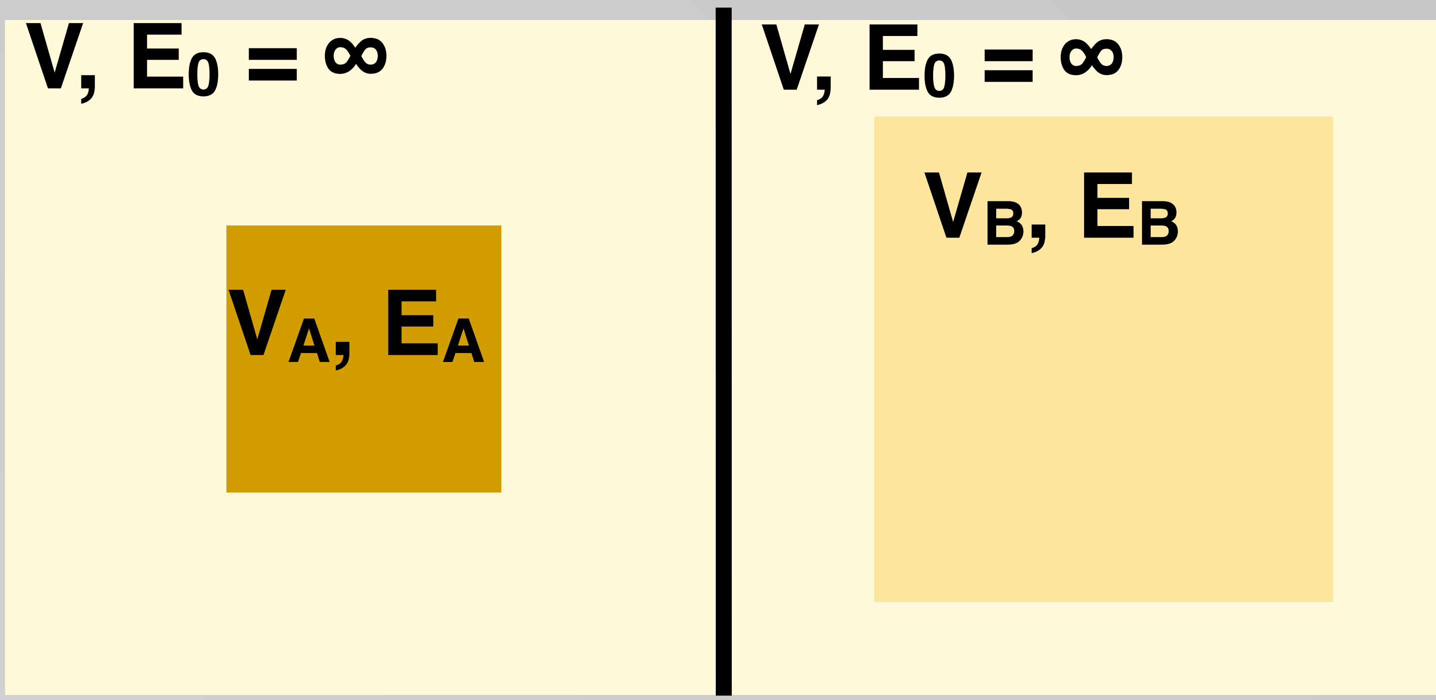
Statistical Mechanics:

The average energy of a CO_2 inserted in a random position in the adsorbent

$$\exp\left(-\frac{\mu^{ex}}{k_B T} \right) = \left\langle e^{-U_{CO_2}/k_B T} \right\rangle_{ads}$$

$$K_H = \frac{1}{k_B T} \left\langle e^{-U_{CO_2}/k_B T} \right\rangle_{ads}$$

Model adsorbent:

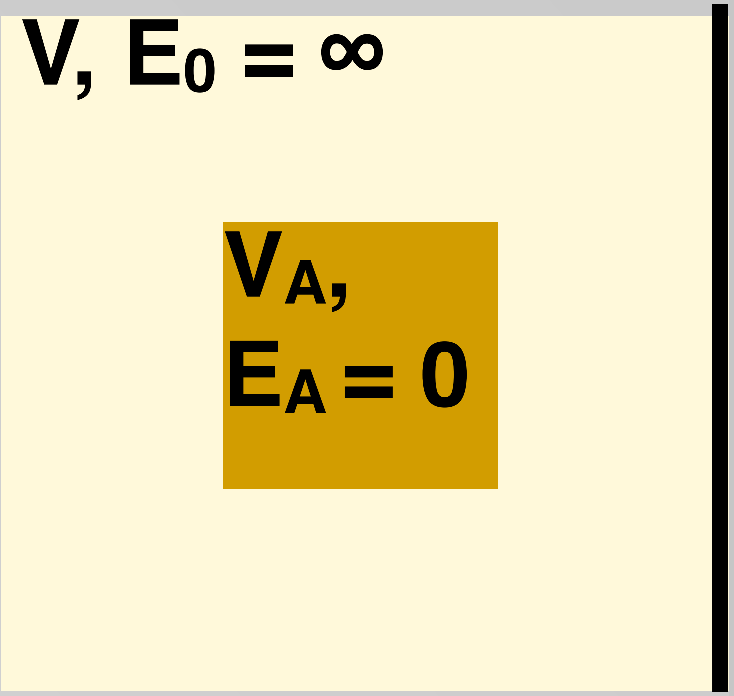


$V = 2V_B = 8V_A$
$E_A = E_B = 0$

Model adsorbate: Ideal gas molecules that feel energy E_i in the pores

Question:

- Which material has the highest Henry coefficient?



$$K_H = \frac{1}{k_B T} \left\langle e^{-U_{CO_2}/k_B T} \right\rangle_{ads}$$

$$K_H^A = \frac{1}{k_B T} \left[\frac{V_A}{V} e^0 + \frac{V - V_A}{V} e^{-\infty} \right] = \frac{V_A}{k_B T V}$$

Let us look at the limit $V_A \rightarrow V$:

$$K_H^A = \frac{1}{k_B T}$$

ideal gas

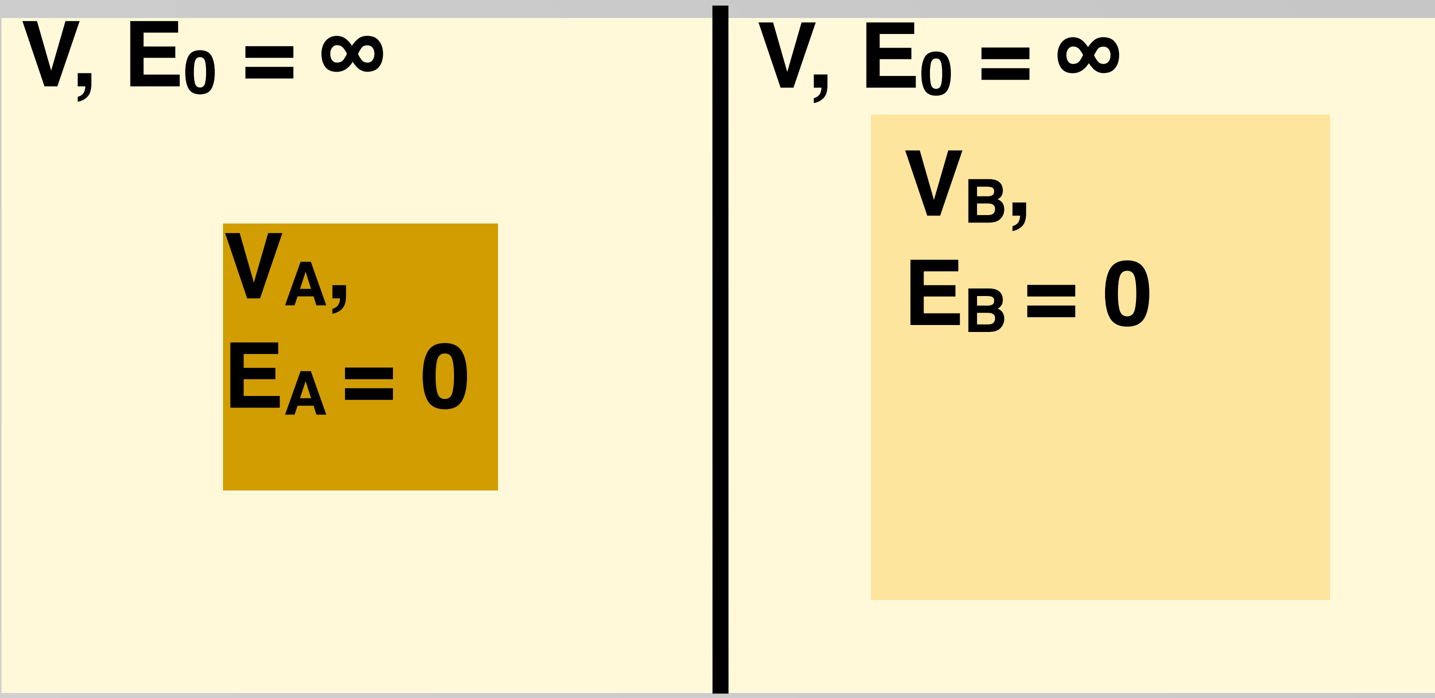
Loading:

$$\sigma = K_H^A p = \frac{p}{k_B T}$$

For $V_A < V$, the loading is:

Entropy loss

$$\sigma = K_H^A p = \frac{p}{k_B T} \frac{V_A}{V}$$



Pore A:

$$K_H^A = \frac{1}{k_B T}\left[\frac{V_A}{V}e^0 + \frac{V - V_A}{V}e^{-\infty}\right] = \frac{V_A}{k_B T V}$$

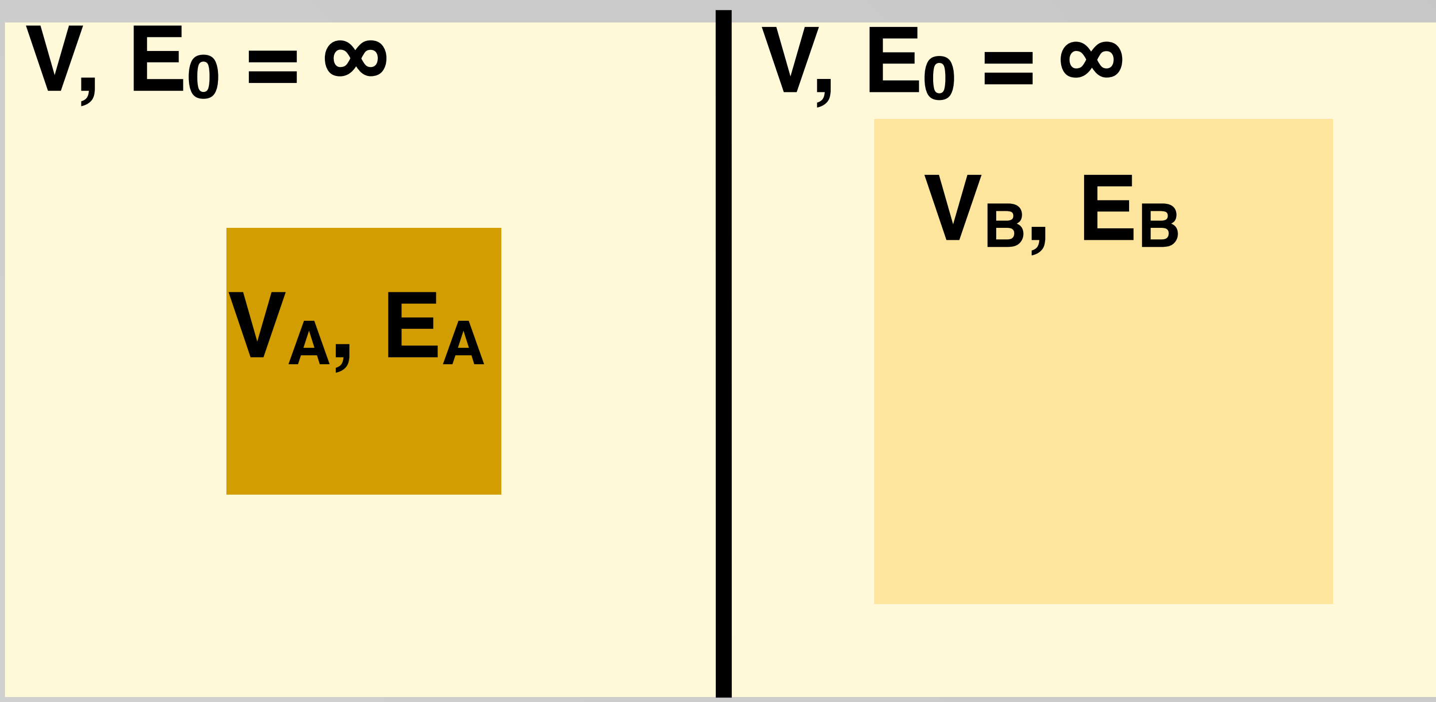
Pore B:

$$K_H^B = \frac{1}{k_B T}\left[\frac{V_B}{V}e^0 + \frac{V - V_B}{V}e^{-\infty}\right] = \frac{V_B}{k_B T V}$$

Ratio of the Henry coefficients:

$$\frac{K_H^B}{K_H^A} = \frac{V_B}{V_A}$$

Model adsorbent:

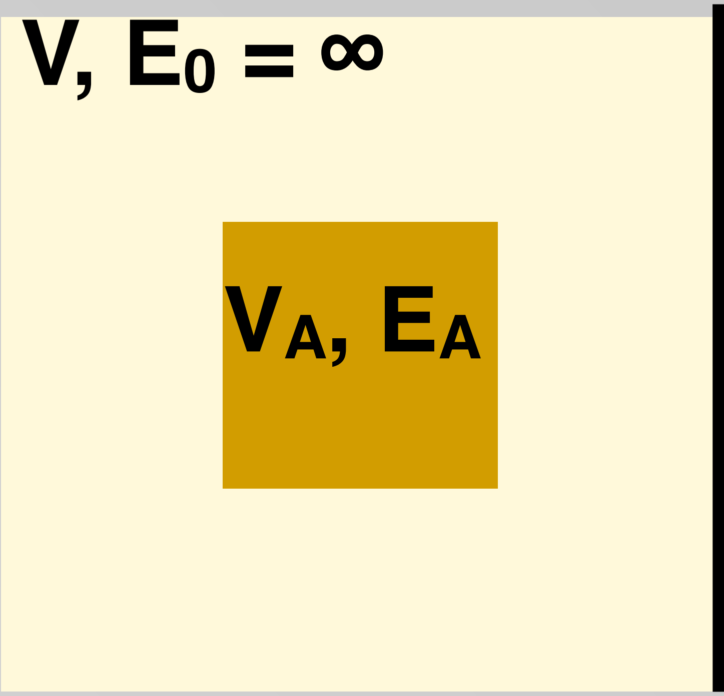


$V = 2V_B = 8V_A$

$E_A = 2E_B = -20$ kJ/mole

Questions:

- At T=0 which material has the highest Henry coefficient?
- At T>> which material has the highest Henry coefficient
- For which temperature the Henry coefficients of the two materials are equal?



$V = 2V_B = 8V_A$

$E_A = 2E_B = -20$ kJ/mole

$$K_H = \frac{1}{k_B T}\left\langle e^{-U_{CO_2}/k_B T} \right\rangle_{ads}$$

Material A:

$$K_H = \frac{1}{k_B T}\left[\frac{V_A}{V} e^{-\frac{E_A}{k_B T}} + \frac{\left(V - V_A\right)}{V} e^{-\frac{\infty}{k_B T}} \right]$$

$$K_H = \frac{1}{k_B T}\frac{V_A}{V_0} e^{-\frac{E_A}{k_B T}}$$

$$k_B T \ln\left(k_B T K_H\right) = -E_A + k_B T \ln\frac{V_A}{V}$$

Energy gain

Entropy loss

Summary

Henry coefficient: balance between the entropy loss caused by the confinement and the energy gain caused by the interactions with the wall