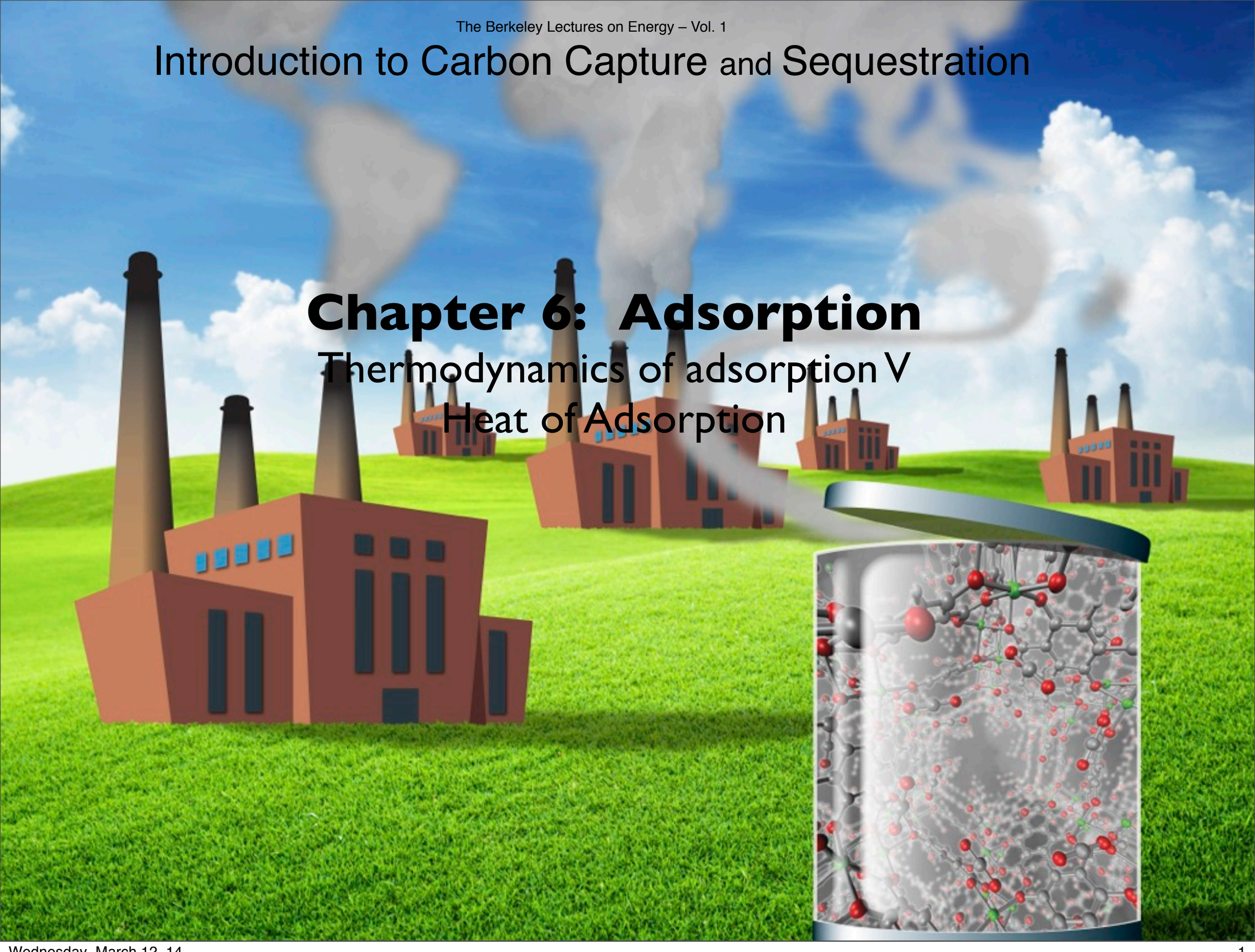
Introduction to Carbon Capture and Sequestration



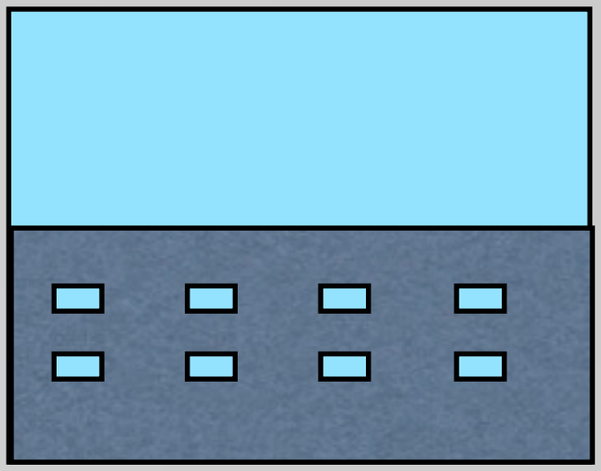
Chapter 6: Adsorption

Thermodynamics of adsorption V

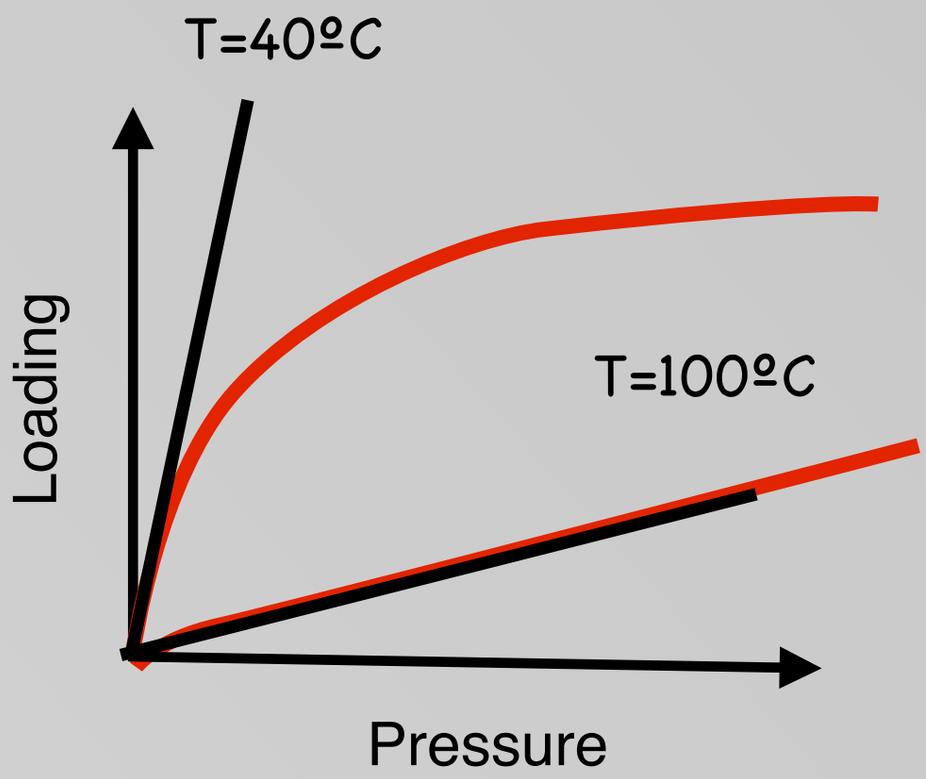
Heat of Adsorption

Chapter 6: Adsorption
Thermodynamics of Adsorption V
(Heat of Adsorption)

- How do we measure the heat of adsorption?
- Why are there different heats of adsorption?



$$K = K_0 \exp\left(-\frac{q_{ad}}{k_B T}\right)$$

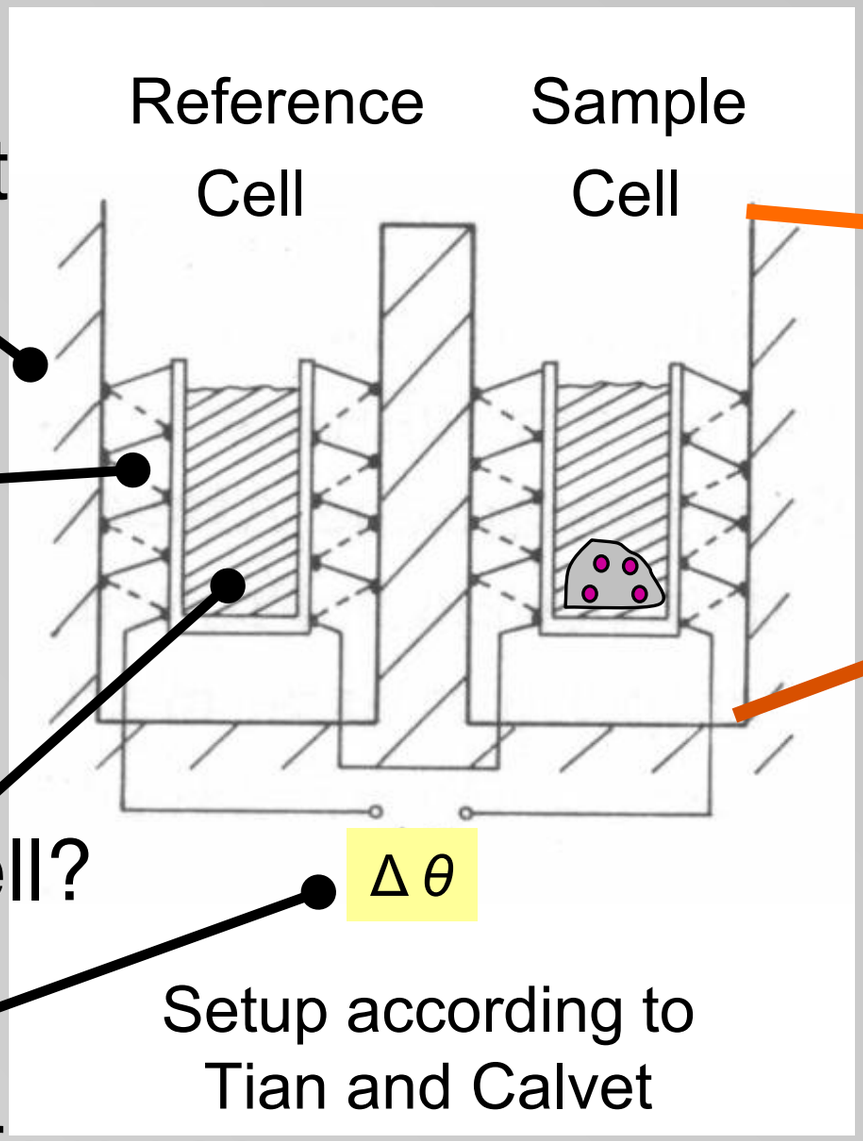


Experiment: microcalorimetry

kept at constant temperature

thermo couples

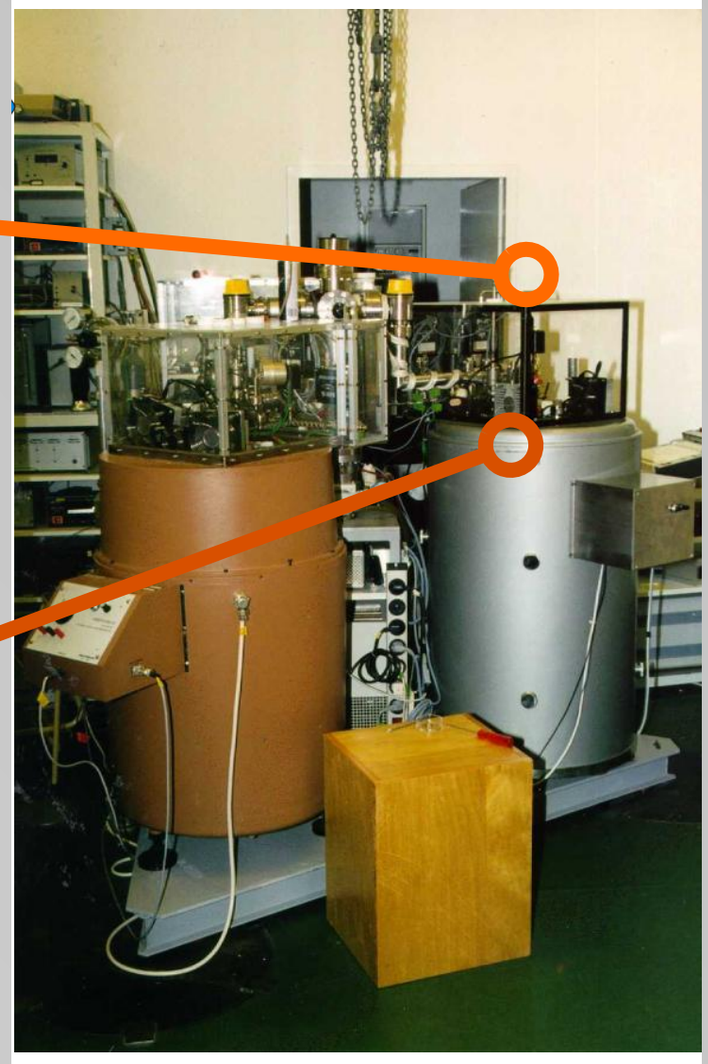
why a reference cell?



Setup according to Tian and Calvet

measure the difference in current generated by the thermo couples

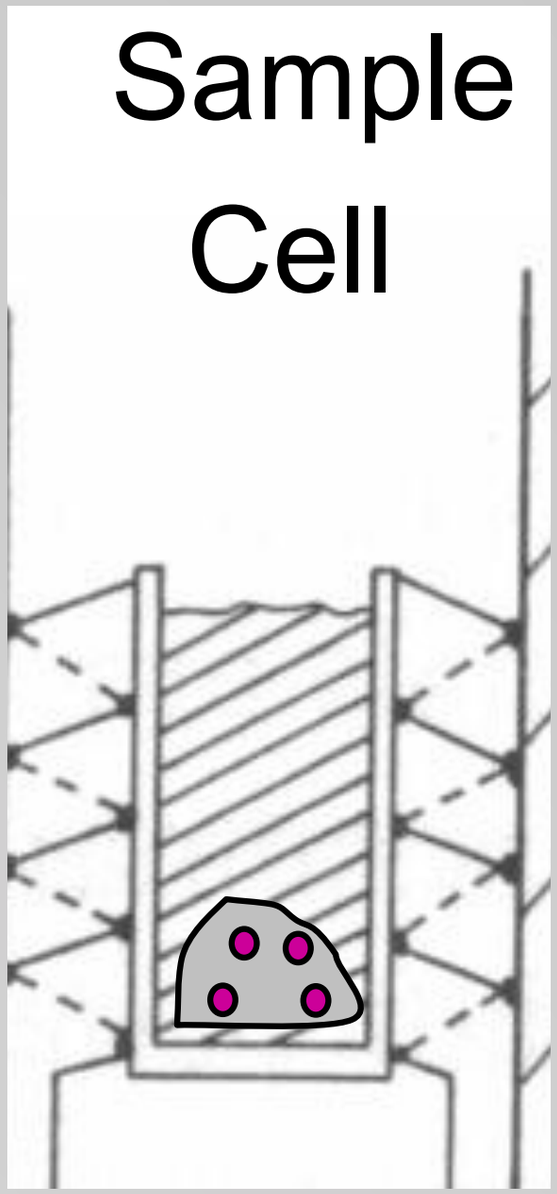
Adsorptive Microcalorimetry



MS 70 Tian-Calvet calorimeter of SETARAM combined with a custom-designed high vacuum and gas dosing apparatus.

Karge, H.G. etal., J. Phys. Chem. 98, 1994, 8053.

Experiment: What do we measure?



Begin: gas + empty sample

End: some gas in sample + heat

In the Google we find:

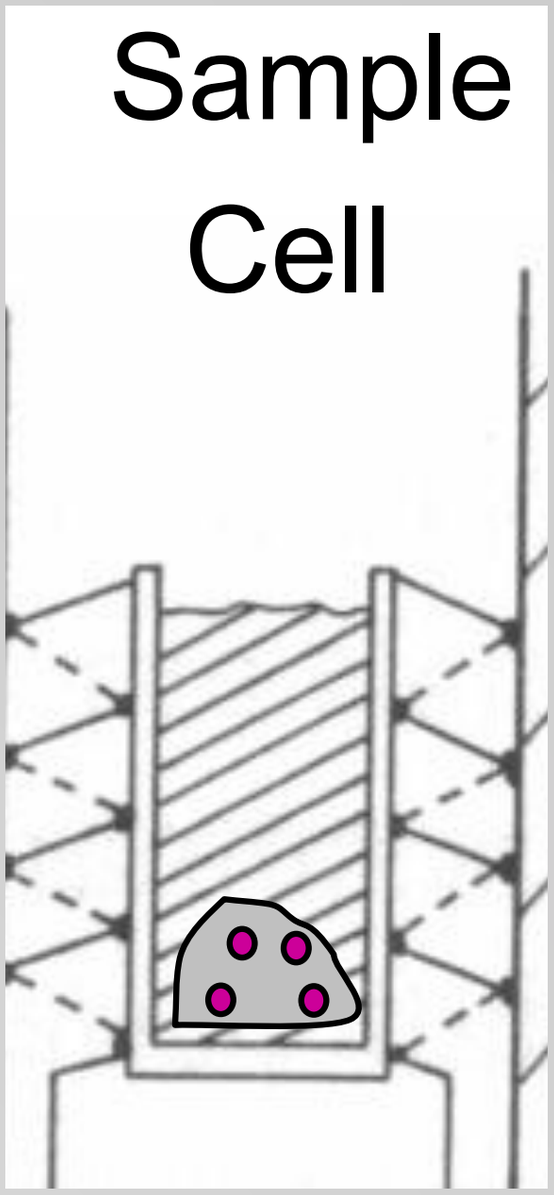
- differential heat of adsorption
- isosteric heat of adsorption

Which one do we measure?

Why are there these differences?

Rule 1 of thermodynamics: Never think you understand it

Rule 2 of thermodynamics: Understand the boundary conditions of the experiment



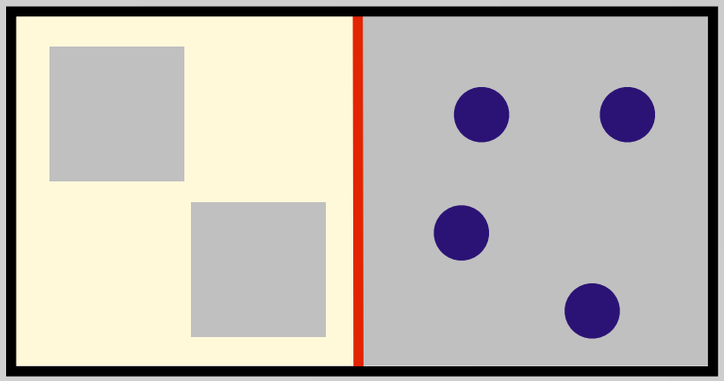
Boundary conditions (which variables are kept constant)

- volume and temperature
  - ----> differential heat of adsorption
- pressure and temperature
  - ----> isosteric heat of adsorption

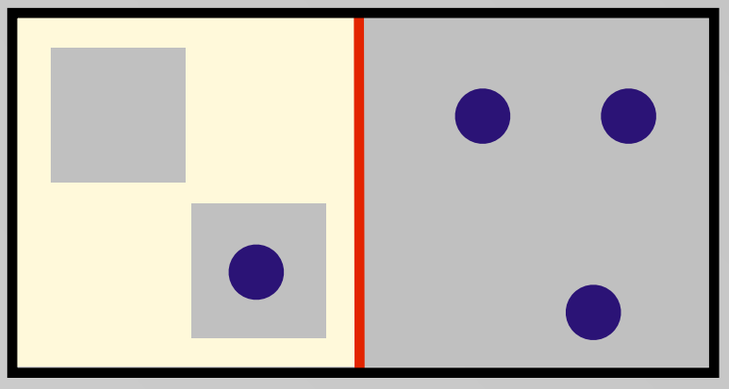
Rule 2 of thermodynamics:

Understand the boundary conditions of the experiment

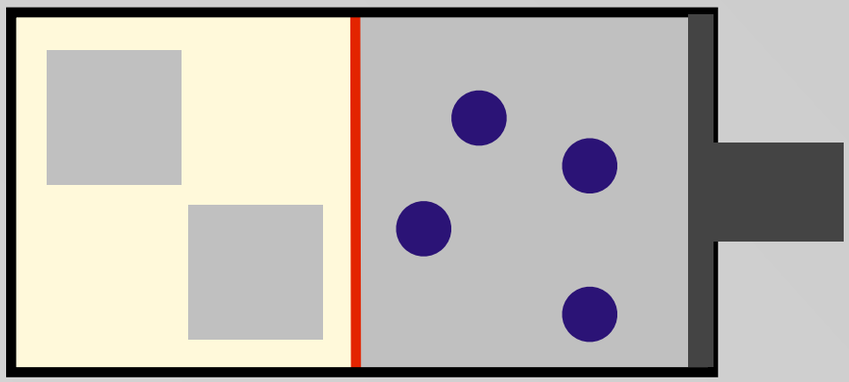
Before

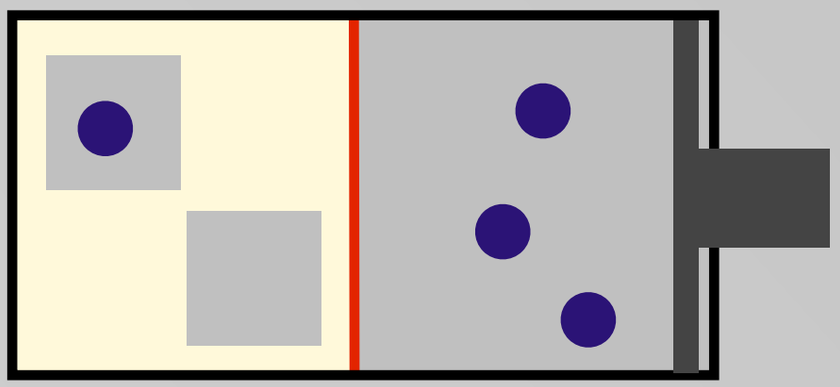


After

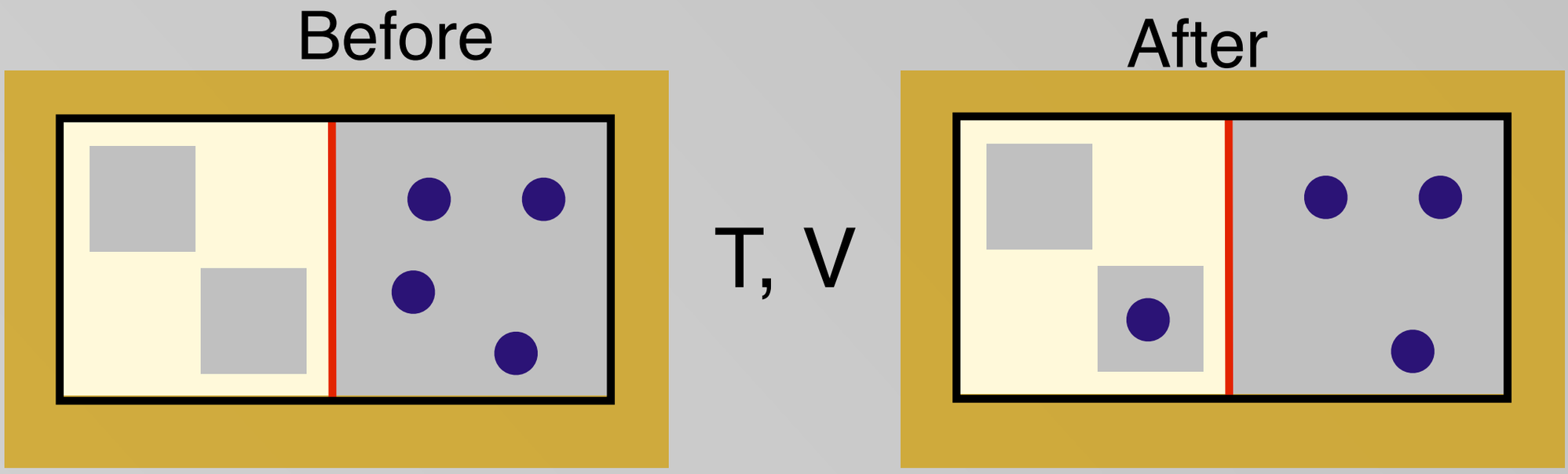


T, V





T, P



Total system is at constant temperature and constant volume

Experiment:

- We start with an empty adsorbate and a gas
- We open the separation and let the system equilibrate
- We measure the heat that is released Q^{isoTV}
- We measure the number of molecules that adsorb: n^A

First law: $$dU = \delta Q + \delta W$$

Volume is constant: no work!

$$\Delta U = -Q^{isoTV}$$

Why the - ?

First law:

$$\Delta U = U^{After} - U^{Before} = -Q^{isoTV}$$

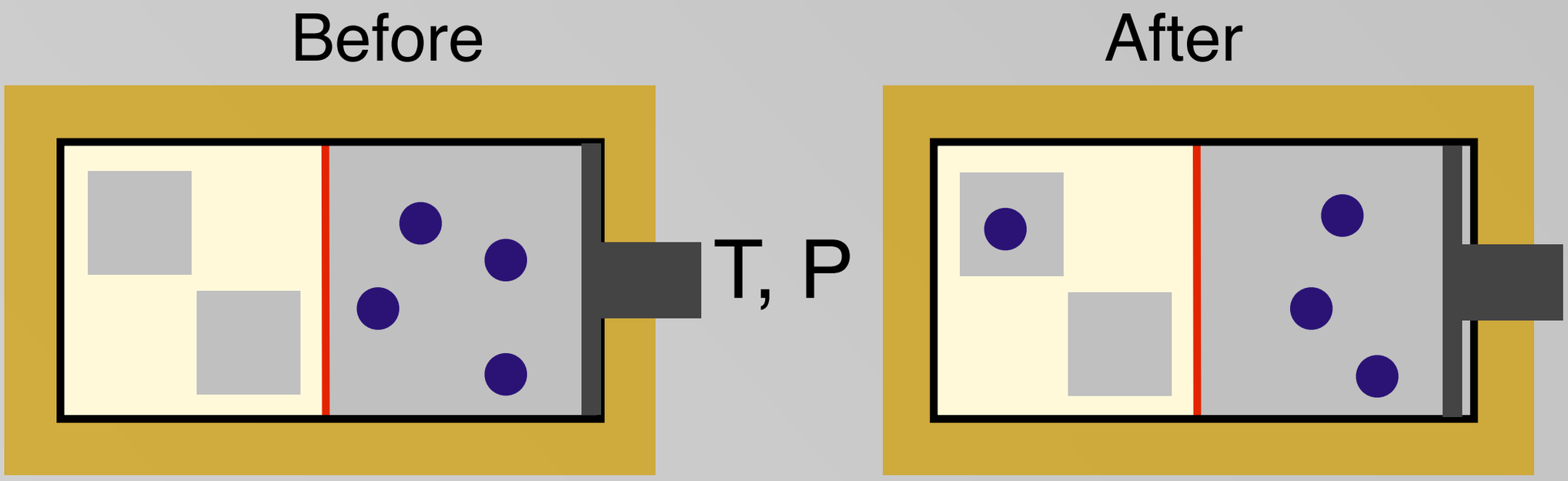
$$\Delta U^{A} + \Delta U^{G} = -Q^{isoTV}$$

$$\Delta U^{A} = n^{A}\left(\Delta u^{A} - \Delta u^{G}\right) = -Q^{isoTV}$$

$$-q^{isoTV} = \frac{-Q^{isoTV}}{n^{A}} = \Delta u^{A} - \Delta u^{G}$$

$$-q^{isoTV} = \Delta u^{A} - \Delta u^{G}$$

Hence **differential heat of adsorption** measures the change in the internal energy if a molecule moves from the gas phase to the adsorbed phase



Total system is at constant temperature and constant pressure

Experiment:

- We start with an empty adsorbate and a gas
- We open the separation and let the system equilibrate, keeping the **pressure constant**
- We measure the heat that is released Q^{iso}
- We measure the number of molecules that adsorb: n^A

First law: $$dU = \delta Q + \delta W$$

Volume is **not** constant: work!

$$\Delta U + p\Delta V = -Q^{iso}$$

First law: $$-Q^{iso} = \Delta U + p\Delta V = \left(U^{After} - U^{Before}\right) + p\left(V^{After} - V^{Before}\right)$$

$$p\Delta V = pV^{After} - pV^{Before} \approx \left(n - n^{A}\right)k_B T - nk_B T$$

$$p\Delta V = -n^{A} RT$$

Ideal gas

Enthalpy: $$H \equiv U + pV$$

$$\Delta H = -Q^{iso}$$

$$-q^{iso} = \frac{-Q^{iso}}{n^{A}} = \Delta h^{A} - \Delta h^{G} \approx \left(\Delta u^{A} - \Delta u^{G}\right) + k_B T$$

Hence **isosteric heat of adsorption** measures the change in the enthalpy if a molecule moves from the gas phase to the adsorbed phase

Summary

We have seen how the heat of adsorption is measured and why different experiments give different heats of adsorption.