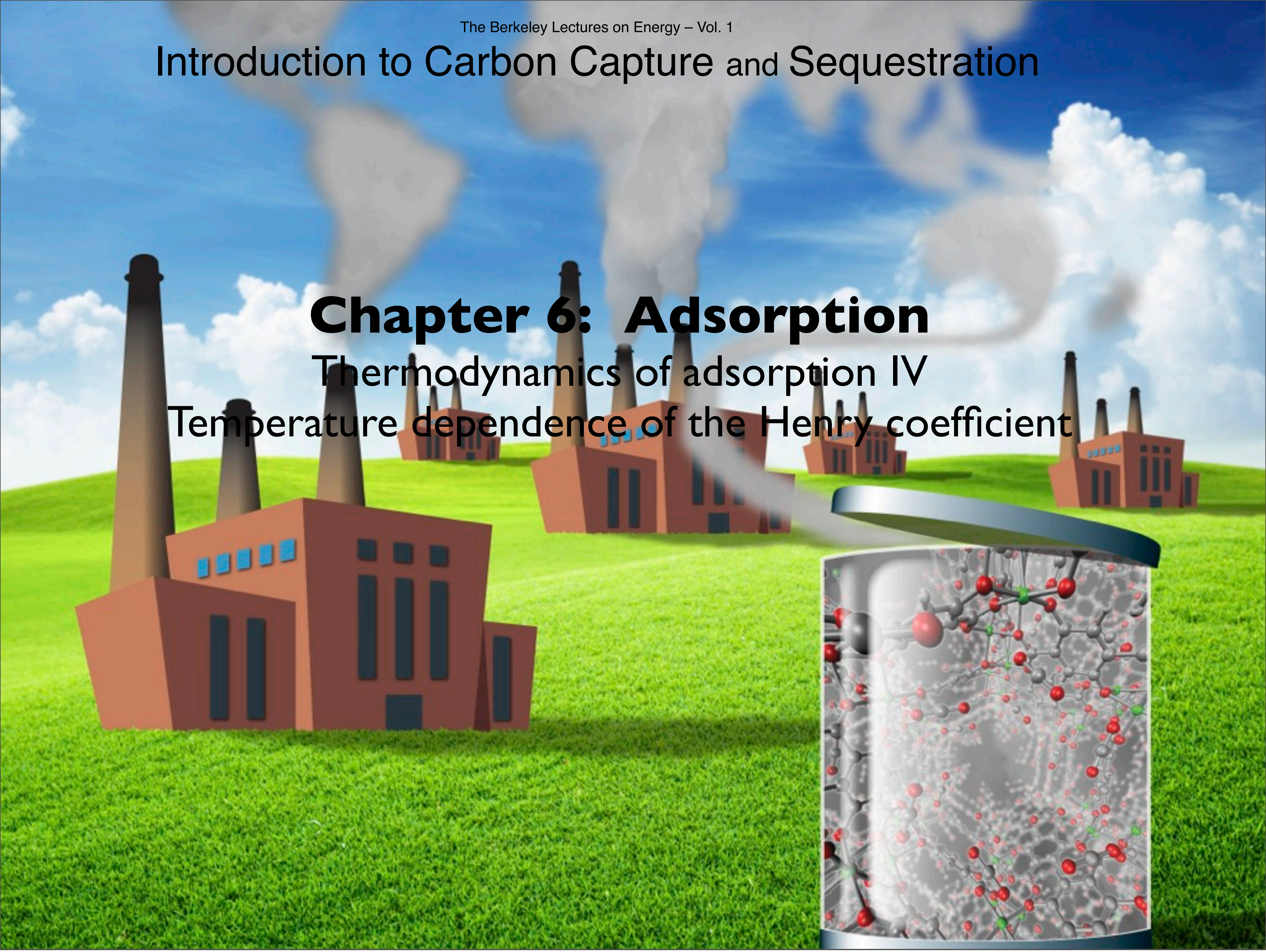
Introduction to Carbon Capture and Sequestration



Chapter 6: Adsorption

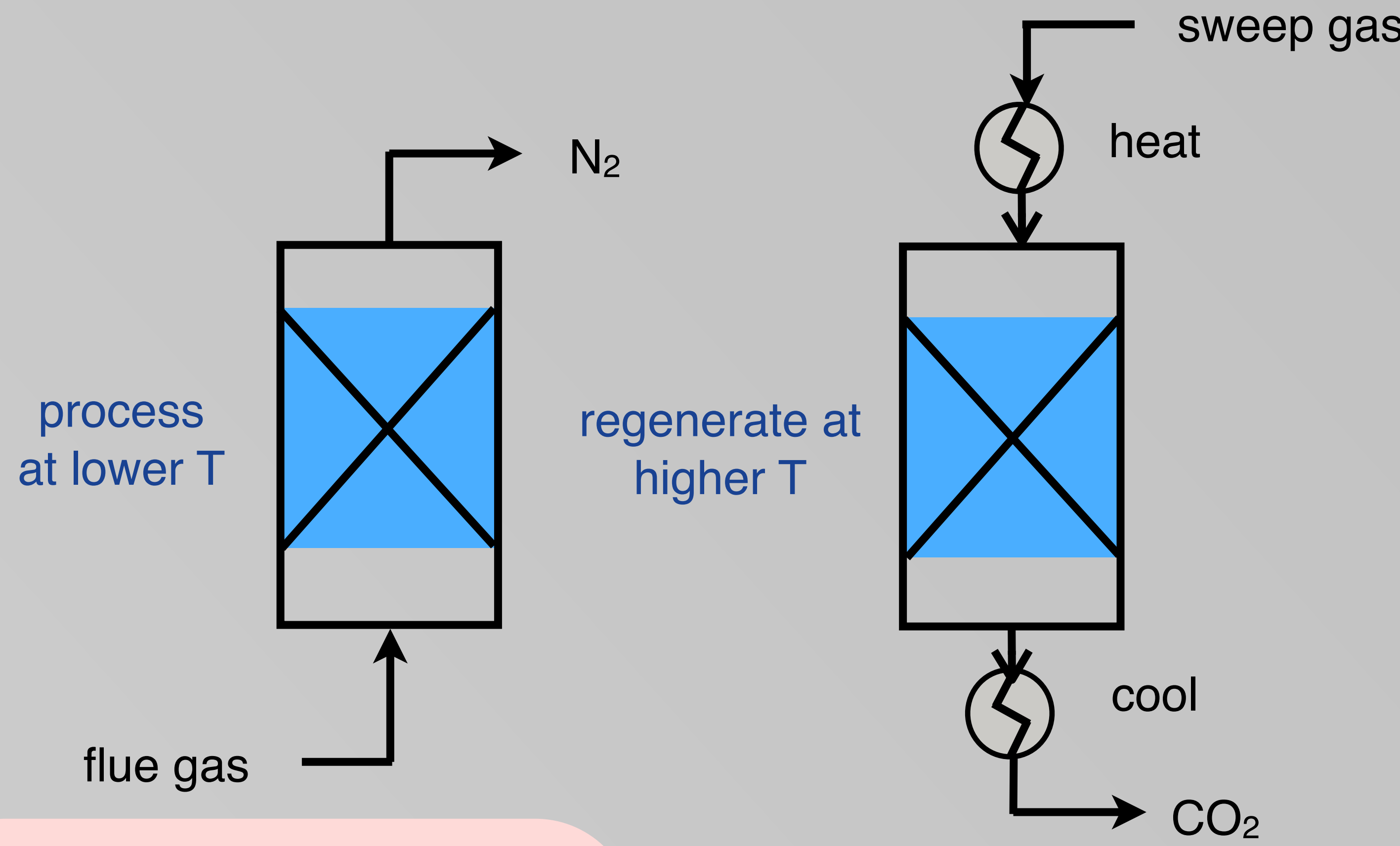
Thermodynamics of adsorption IV

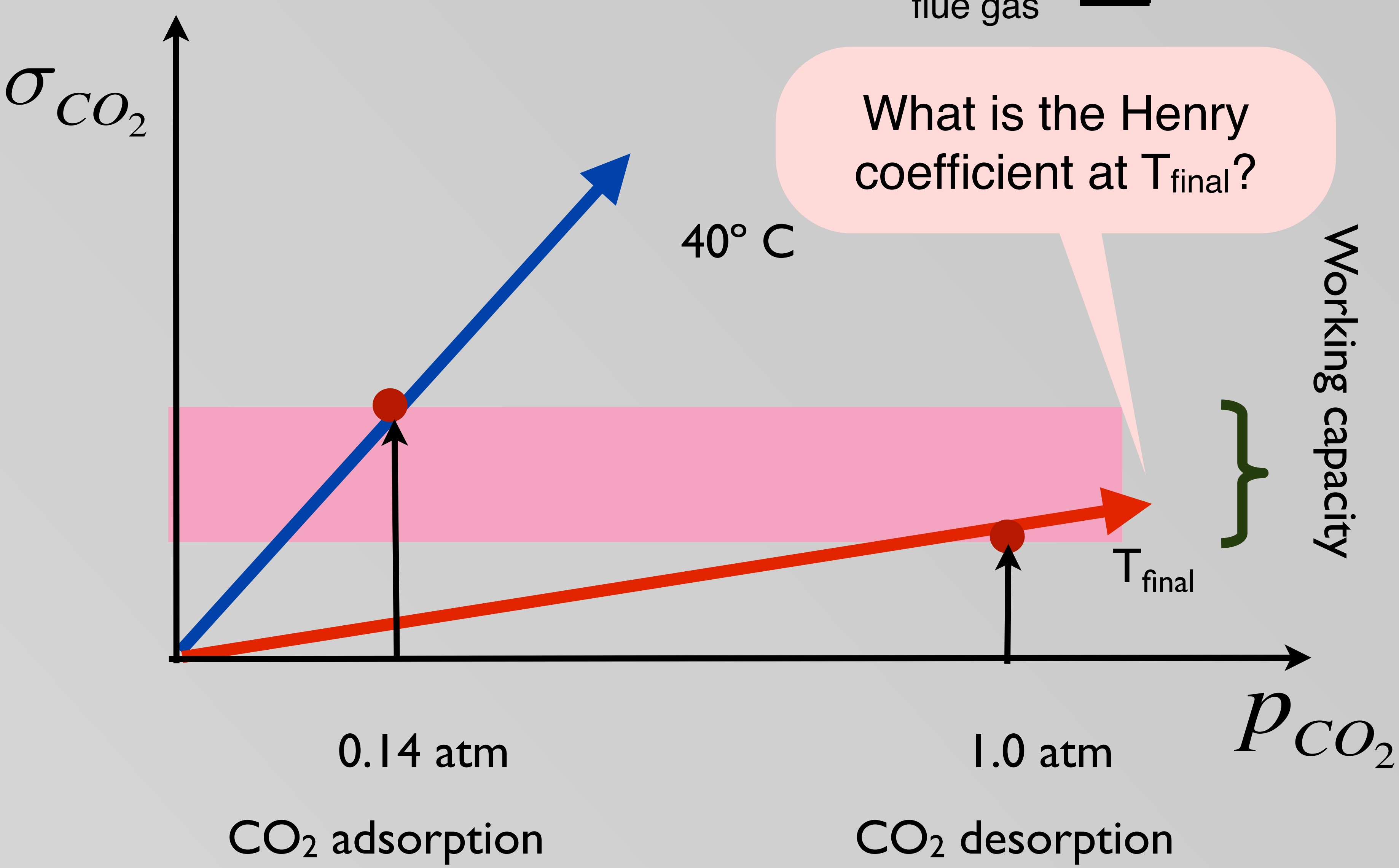
Temperature dependence of the Henry coefficient

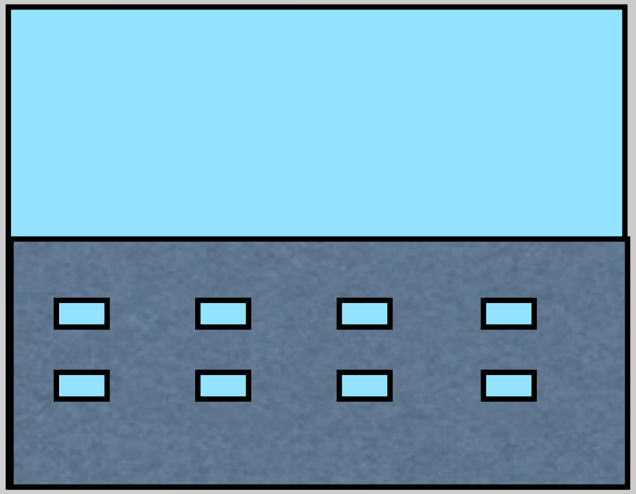
Chapter 6: Adsorption
Thermodynamics of Adsorption IV
(Temperature dependence of the Henry coefficient)

- If we change the temperature how does the Langmuir isotherm change?

temperature swing adsorption







How does equilibrium changes if we change the conditions?

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

for the gas phase:

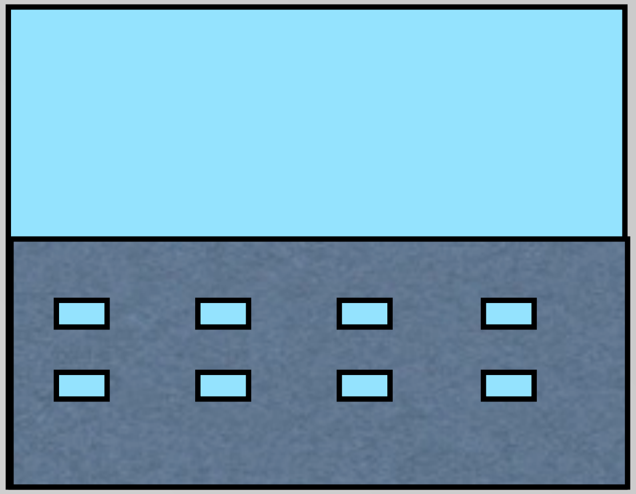
$$d\left(\mu_{CO_2}^{gas}(T,p)/T\right) = \left(\frac{\partial \mu_{CO_2}^{gas}(T,p)/T}{\partial T}\right)_p dT + \left(\frac{\partial \mu_{CO_2}^{gas}(T,p)/T}{\partial p}\right)_T dp$$

for the adsorbed phase:

$$d\left(\mu_{CO_2}^{ads}(T,\sigma)/T\right) = \left(\frac{\partial \mu_{CO_2}^{ads}(T,\sigma)/T}{\partial T}\right)_\sigma dT + \left(\frac{\partial \mu_{CO_2}^{ads}(T,\sigma)/T}{\partial \sigma}\right)_T d\sigma$$

We need to compute these contributions

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



Gas phase

$$d\left(\mu_{CO_2}^{gas}(T,p)/T\right) = \left(\frac{\partial \mu_{CO_2}^{gas}(T,p)/T}{\partial T}\right)_p dT + \left(\frac{\partial \mu_{CO_2}^{gas}(T,p)/T}{\partial p}\right)_T dp$$

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with

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

Easy:

$$\left(\frac{\partial \mu_{CO_2}^{gas}/T}{\partial p}\right)_T = \frac{k_B}{p}$$

Almost easy:

$$\left(\frac{\partial \mu_{CO_2}^{gas}/T}{\partial T}\right)_P = -\frac{h^{IG}}{T^2}$$

... thermodynamics

Thermodynamics recall ....

heat

work

adding molecules

First law: $dU = TdS - pdV + \mu dN$

Enthalpy: $H \equiv U + pV$

Gibbs free energy: $G \equiv U - TS + pV$

Chemical potential (molar Gibbs free energy): $\mu = \dfrac{G}{N} \equiv u - Ts + pv$

$$\mu = h - Ts$$

$$dG = dU - d(TS) + d(pV)$$

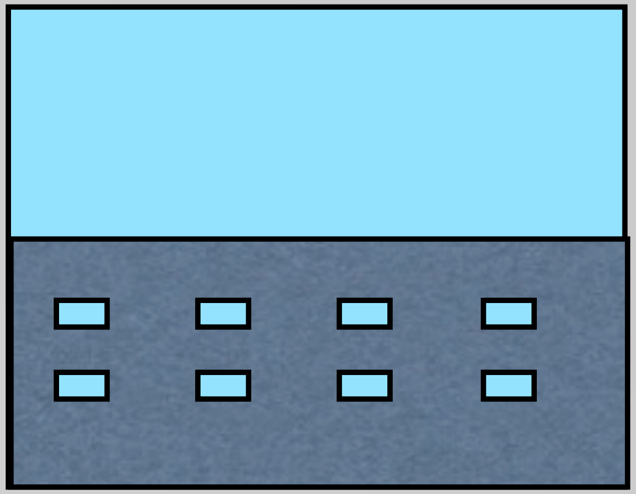
$$dG = -SdT + Vdp + \mu dN$$

Maxwell relation $\left(\dfrac{\partial^2 G}{\partial T\,\partial N}\right) = \left(\dfrac{\partial^2 G}{\partial N\,\partial T}\right)$ $\left(\dfrac{\partial \mu}{\partial T}\right)_{N.p} = -\left(\dfrac{\partial S}{\partial N}\right)_{T,p}$

$$\left(\frac{\partial \mu}{\partial T}\right)_{N.p} = -s = \frac{\mu - h}{T}$$

or

$$\left(\frac{\partial \mu/T}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial \mu}{\partial T}\right)_p - \frac{\mu}{T^2} = -\frac{h}{T^2}$$



How does equilibrium changes if we increase the temperature?

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

$$d\left(\mu_{CO_2}^{gas}(T,p)/T\right) = \left(\frac{\partial\mu_{CO_2}^{gas}(T,p)/T}{\partial T}\right)_p dT + \left(\frac{\partial\mu_{CO_2}^{gas}(T,p)/T}{\partial p}\right)_T dp$$

with

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

for the gas phase, which gives

$$\left(\frac{\partial\mu^{IG}/T}{\partial p}\right)_{N.p} = \frac{k_B}{p}$$

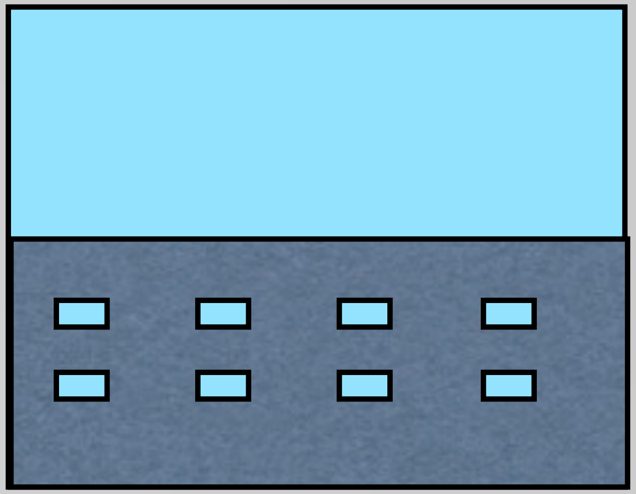
Thermodynamics:

$$\left(\frac{\partial\mu^{IG}/T}{\partial T}\right)_{N.P} = -\frac{h^{IG}}{T^2}$$

Which gives for the change in equilibrium conditions:

$$d\left(\mu_{CO_2}^{gas}(T,p)/T\right) = -\frac{h^{IG}}{T^2}dT + \frac{k_B}{p}dp$$

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



Adsorbed phase

$$d\left(\mu_{CO_2}^{ads}(T,\sigma)/T\right)=\left(\frac{\partial\mu_{CO_2}^{ads}(T,\sigma)/T}{\partial T}\right)_{\sigma}dT+\left(\frac{\partial\mu_{CO_2}^{ads}(T,\sigma)/T}{\partial\sigma}\right)_{T}d\sigma$$

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with

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

Easy:

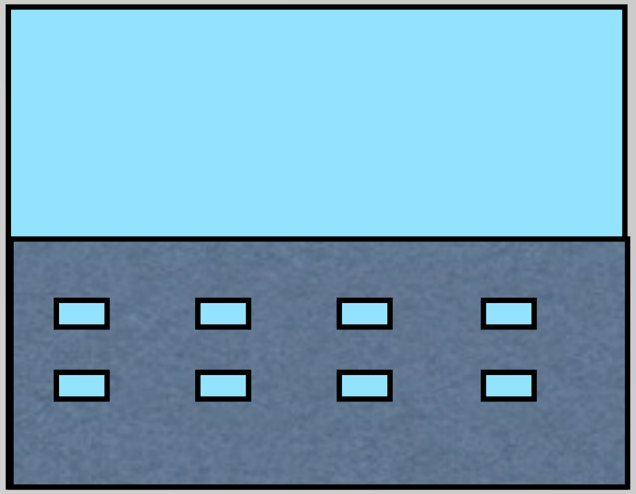
$$\left(\frac{\partial\mu^{ads}/T}{\partial\sigma}\right)_{T}=\frac{k_B}{\sigma}$$

Thermodynamics:

$$\left(\frac{\partial\mu^{ads}/T}{\partial T}\right)_{\rho}=-\frac{h^{ads}}{T^2}$$

Which gives for the change in equilibrium conditions:

$$d\left(\mu_{CO_2}^{ads}(T,\sigma)/T\right)=-\frac{h^{ads}}{T^2}dT+\frac{k_B}{\sigma}d\sigma$$



Gas phase

$$d\left(\mu_{CO_2}^{gas}(T,p)/T\right) = -\frac{h^{IG}}{T^2}dT + \frac{k_B}{p}dp$$

For the adsorbed phase:

$$d\left(\mu_{CO_2}^{ads}(T,\sigma)/T\right) = -\frac{h^{ads}}{T^2}dT + \frac{k_B}{\sigma}d\sigma$$

Equilibrium if:

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

$$-\frac{h^{IG}}{T^2}dT + \frac{k_B}{p}dp = -\frac{h^{ads}}{T^2}dT + \frac{k_B}{\sigma}d\sigma$$

$$k_B d\left(\frac{\ln\sigma}{\ln p}\right) = \frac{\left(h^{ads} - h^{IG}\right)}{T^2}dT$$

$$\frac{d\ln K}{dT} = \frac{q_{ads}}{k_B T^2}$$

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

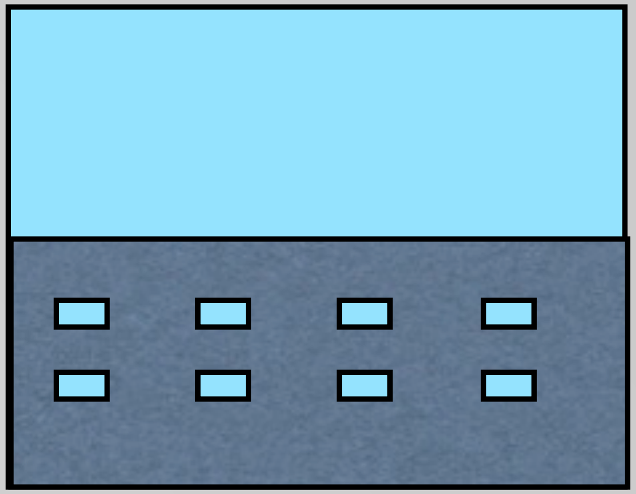
Heat of adsorption:

$$q_{ads} \equiv h^{ads} - h^{IG}$$

(Assume q_{ads}=constant)

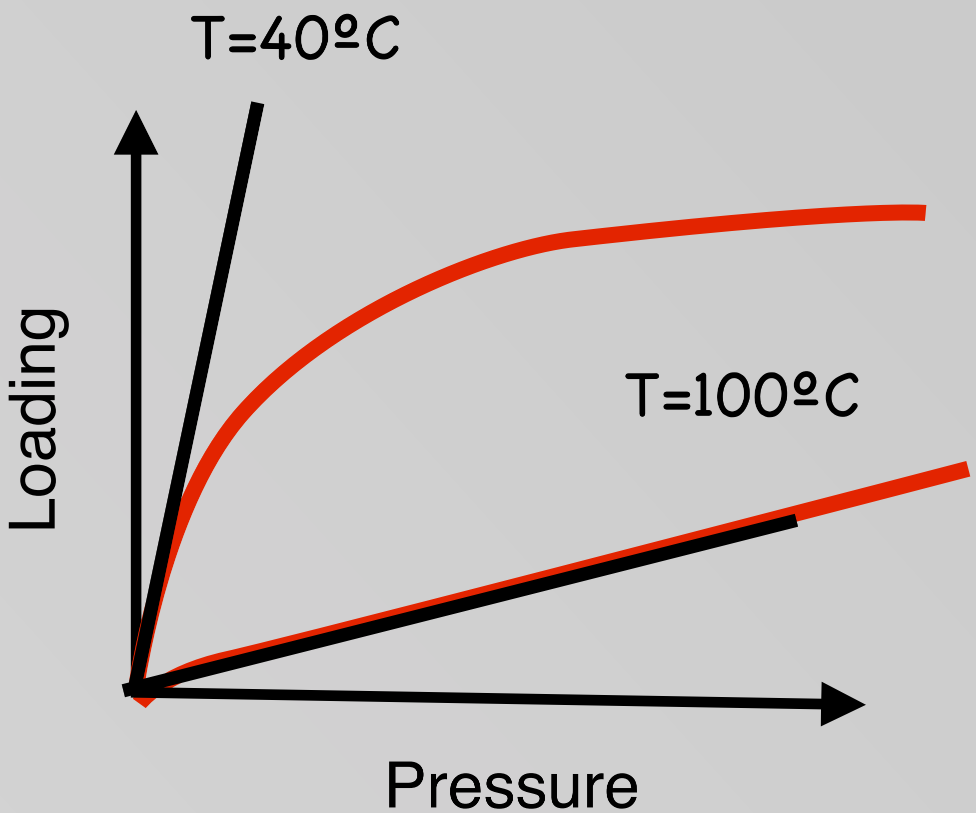
Henry's law

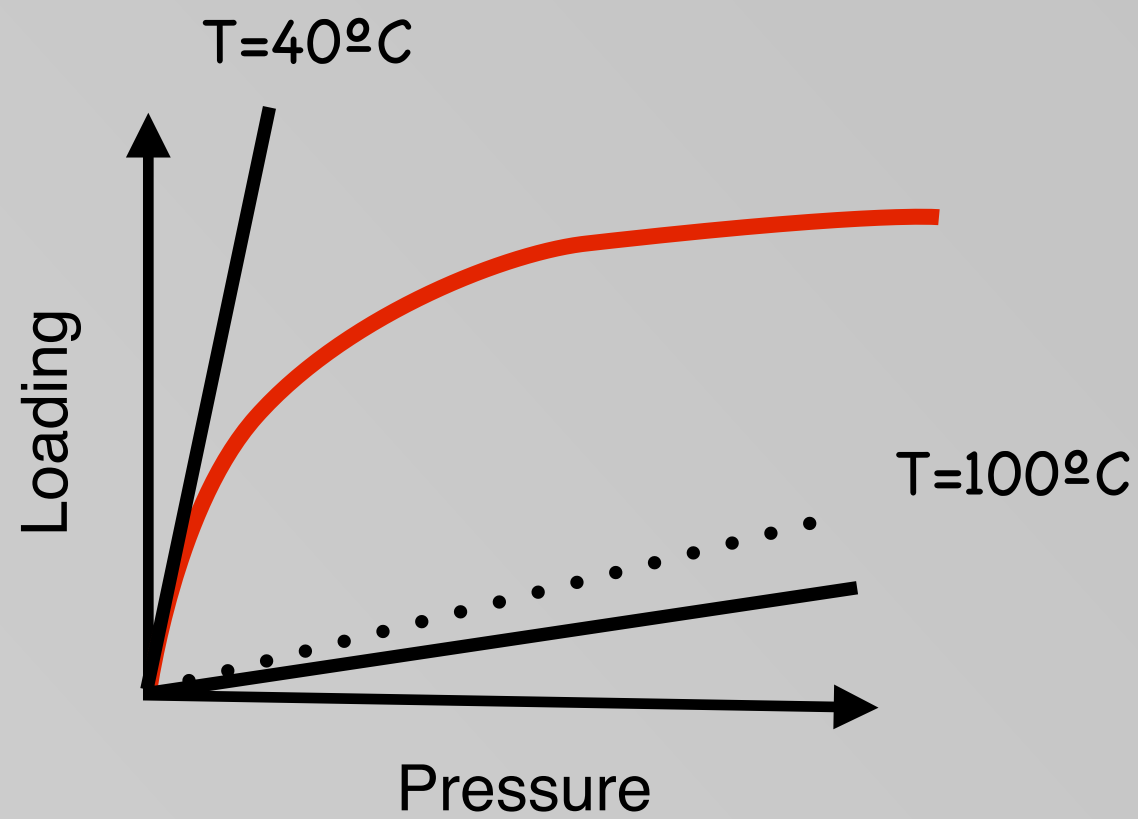
$$\sigma = K_H p$$



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

Higher heat of adsorption





... larger difference between the Henry coefficients at high and low temperatures!

Summary

If we know the heat of adsorption we can predict the temperature dependence of the Henry coefficient