Entropy change caused by adsorption of the gas: $\Delta S_{ad} < 0$

Entropy change caused by heating of the surface: $\Delta S_{surf} = \frac{-\Delta H_{ad}}{T_{surf}}$

Entropy change of the universe = $\Delta S_{tot} = \Delta S_{ad} + \Delta S_{surf} = \Delta S_{ad} - \frac{\Delta H_{ad}}{T_{surf}}$

The Second Law requires a net increase in entropy. Therefore,

$$\Delta S_{ad} - \frac{\Delta H_{ad}}{T_{surf}} > 0$$

$$T_{surf} \Delta S_{ad} > \Delta H_{ad}$$

This condition may be satisfied with both $\Delta S_{ad} < 0$ and $\Delta H_{ad} < 0$, such that

$$|\Delta H_{ad}| > T_{surf} |\Delta S_{ad}|.$$

We can also determine the sign of the change of the free energy:

$$\Delta G_{ad} = \Delta H_{ad} - T_{surf} \Delta S_{ad} < 0,$$

as it should be.

What about energy and enthalpy?

$$\Delta H_{ad} = \Delta U_{ad} - \Delta(PV) = \Delta U_{ad} - V\Delta P$$

If the chamber volume is very large (so that the fraction of gas adsorbed is very small), then the amount of gas adsorbed on the surface will have little effect on the pressure. In the limit of a very large chamber,

$$\Delta H_{ad} = \Delta U_{ad},$$

vindicating the drawing in class. If the chamber is very small (or if the initial pressure is very low), the ambient pressure will fall as a result of adsorption. The maximum possible pressure drop is 100%, so that the molar energy is bounded by

$$\Delta H_{ad} \le \Delta U_{ad} \le \Delta H_{ad} + RT_{surf}.$$