Physical Chemistry (Chem 132A)

Lecture 5
Monday, October 9

Homework #2 (WebAssign)
Due Saturday, October 14.

Joule—Thompson Effect

How does the enthalpy (H) vary with p and T?

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_P dT = \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT$$
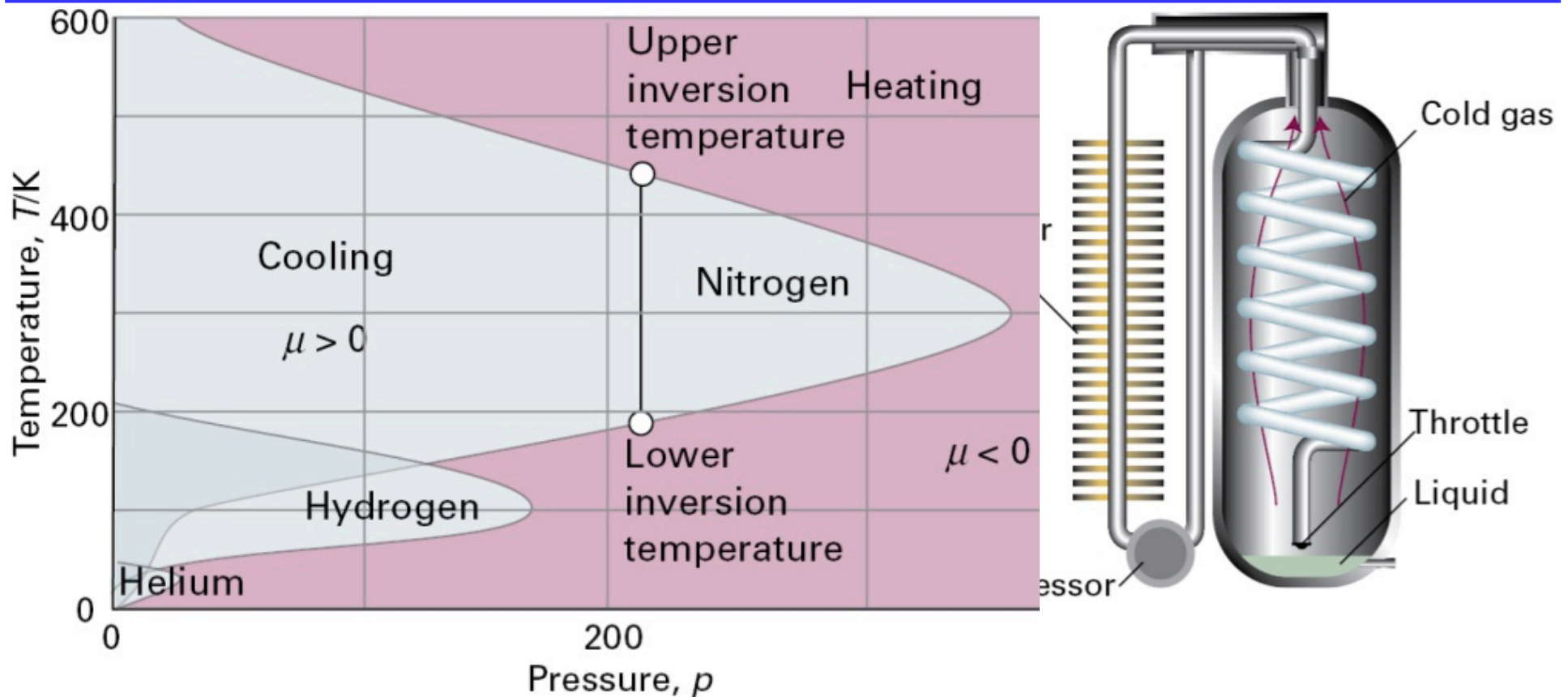
What happens if dH = 0 (an isenthalpic process)

$$\left(\frac{\partial H}{\partial p}\right)_T dp = -C_p dT$$

Divide both sides of eq by dp

$$\left(\frac{\partial H}{\partial p}\right)_T = -C_p \left(\frac{\partial T}{\partial p}\right)_H = -C_p \mu$$

μ is the Joule-Thompson coefficient

μ > 0 means cooling

Molecular basis of "inversion" temperatures:
$\mu > 0$ attractive interactions are dominant
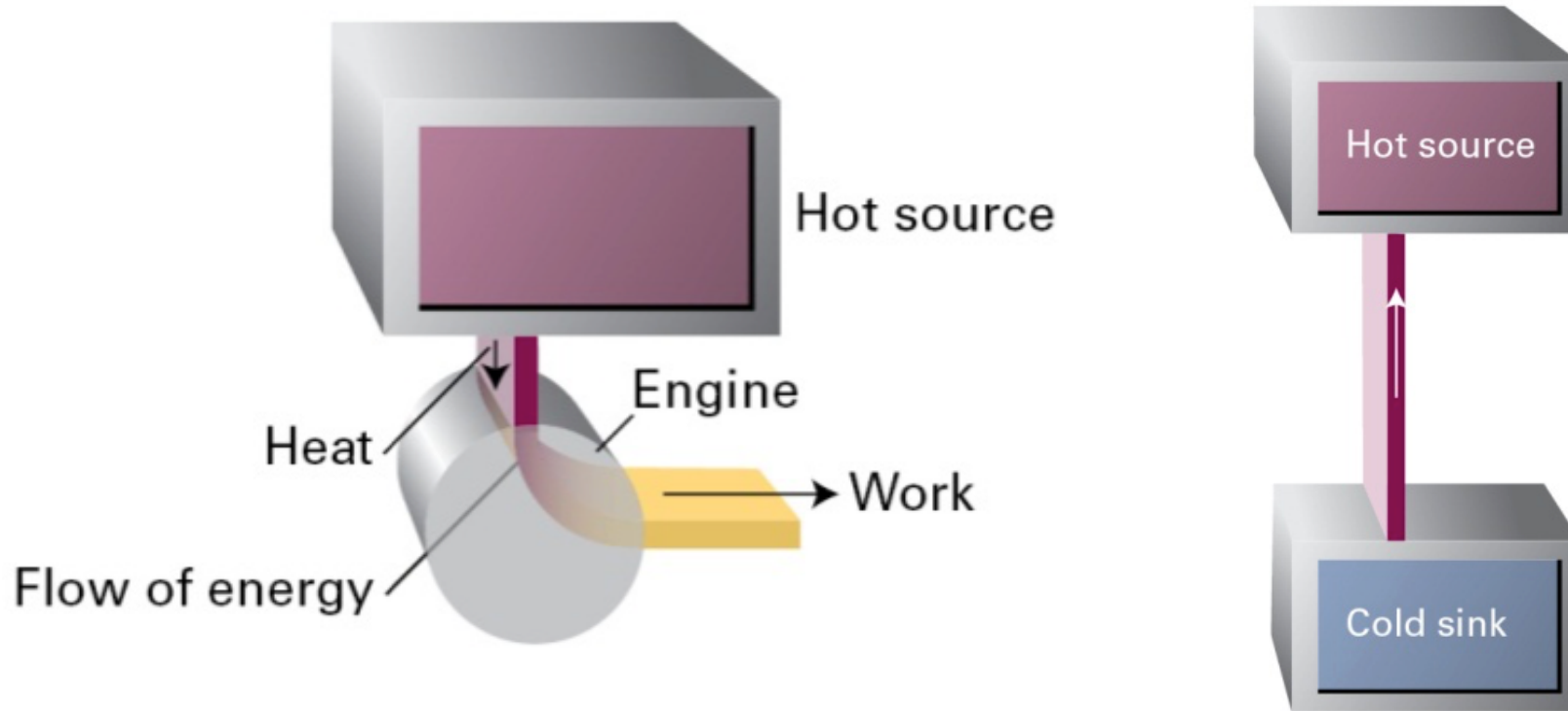$\mu < 0$ repulsive interactions are dominant

Entropy, Another State Function

$$dS = \frac{dq_{reversible}}{T}$$

$$\Delta S = \int_{i}^{f} \frac{dq_{rev}}{T}$$

Second Law of Thermodynamics

"Heat does not flow spontaneously from a cool body to a hotter body"

"No process is possible in which the sole result is the absorption of heat from a reservoir and its <u>complete</u> conversion into work"

"The Entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{total} > 0$"
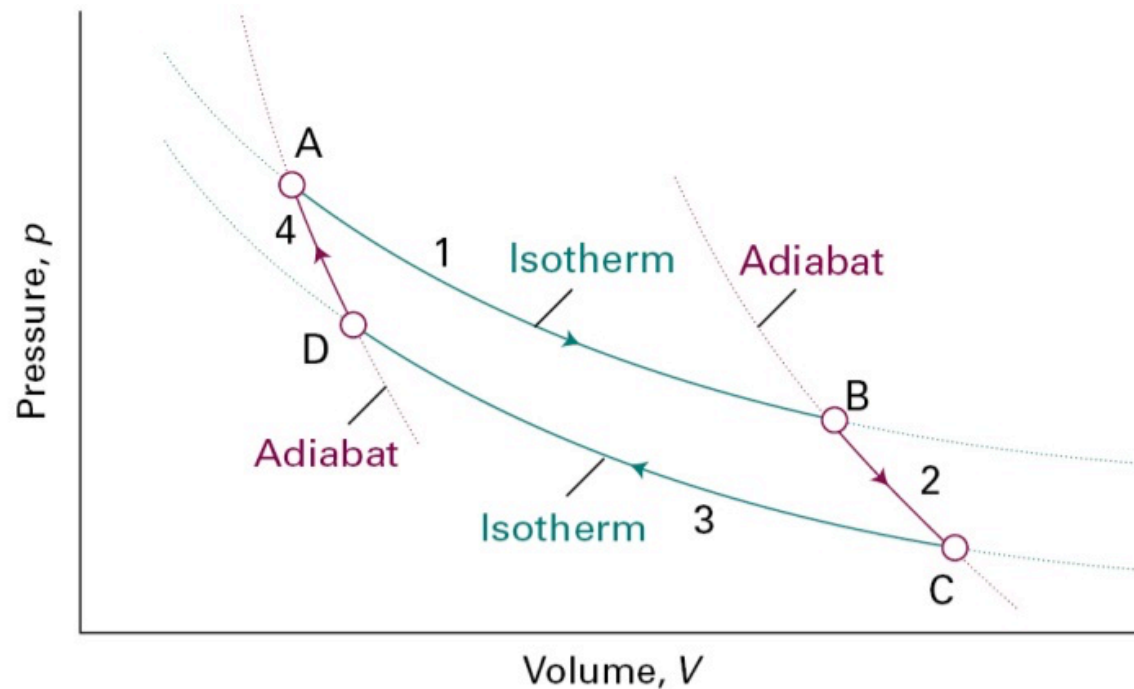
Boltzman definition of Entropy

$$S = k \cdot \ln(W)$$

W is the number of "microstates" of the system

Concept of "disorder" associated with entropy

Carnot Cycles

1. Isothermal, reversible expansion at T_h
2. Reversible, adiabatic expansion, to lower temperature T_c
3. Isothermal, reversible compression at T_c
4. Adiabatic, reversible compression, back to original state

$\Delta S = 0$

Entropy change associated with phase changes

A change of phase at the phase transition temperature is REVERSIBLE

$$\Delta_{trs}S = q_{rev}/T_{trs}$$

At constant pressure:

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

Change in S with heating

$$\Delta S = \int_{initial}^{final} \frac{dq_{rev}}{T}$$

$$S_f - S_i = \int_{initial}^{final} \frac{dq_{rev}}{T}$$

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

$$S(T_f) = S(T_i) + C_p \ln \frac{T_f}{T_i}$$

Third Law of Thermodynamics

The entropy of all perfect crystalline substances is zero at T=0.

This implies that one can in principle determine an ABSOLUTE value for the entropy of a substance at some other temperature.

First Law of Thermodynamics

THE INTERNAL ENERGY OF AN ISOLATED SYSTEM IS CONSTANT

Unlike the First Law of Thermodynamics, the Second Law can tell us about the **spontaneous direction** of a process.

THE END

SEE YOU Wednesday