Physical Chemistry (Chem 132A)

Lecture 4
Friday, October 6

Homework #1 (WebAssign) due on Saturday (11:59Pm)
Grade will be for course credit

Homework #2 (WebAssign) will be available Saturday, 11:59Pm
Due Saturday, October 14.

Equations from last lecture

$$H \equiv U + pV$$

$$\Delta H = q_p$$

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$$

$$\Delta H = \int_{T_1}^{T_2} C_p\, dT = C_p \Delta T$$ **C_p independent of T**

$$\Delta_r H^0 = \sum_{\text{Products}} \nu \Delta_f H^0 - \sum_{\text{Reactants}} \nu \Delta_f H^0$$

$$\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^0\, dT$$

$$\Delta_r C_p^0 = \sum_{\text{products}} \nu C_p^0 - \sum_{\text{reactants}} \nu C_p^0$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = \pi_T dV + C_V dT$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V = \pi_T \alpha V + C_V$$

Where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ **Is the expansion coef.**

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)

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

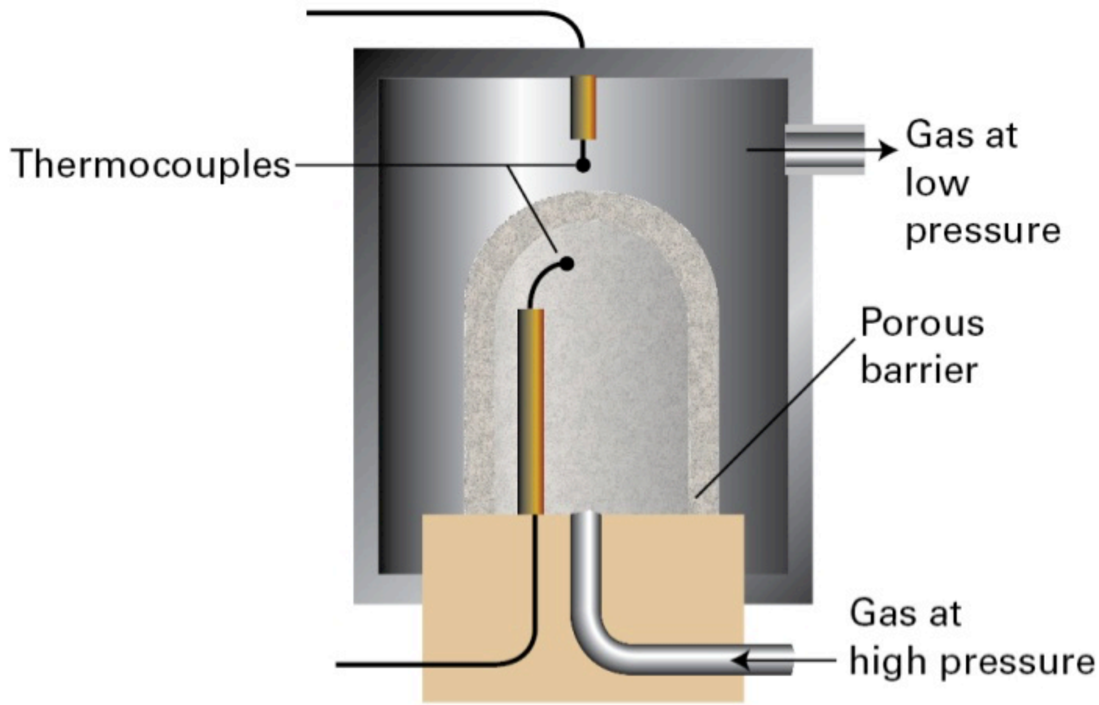
Divide both sides of eq by dp

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

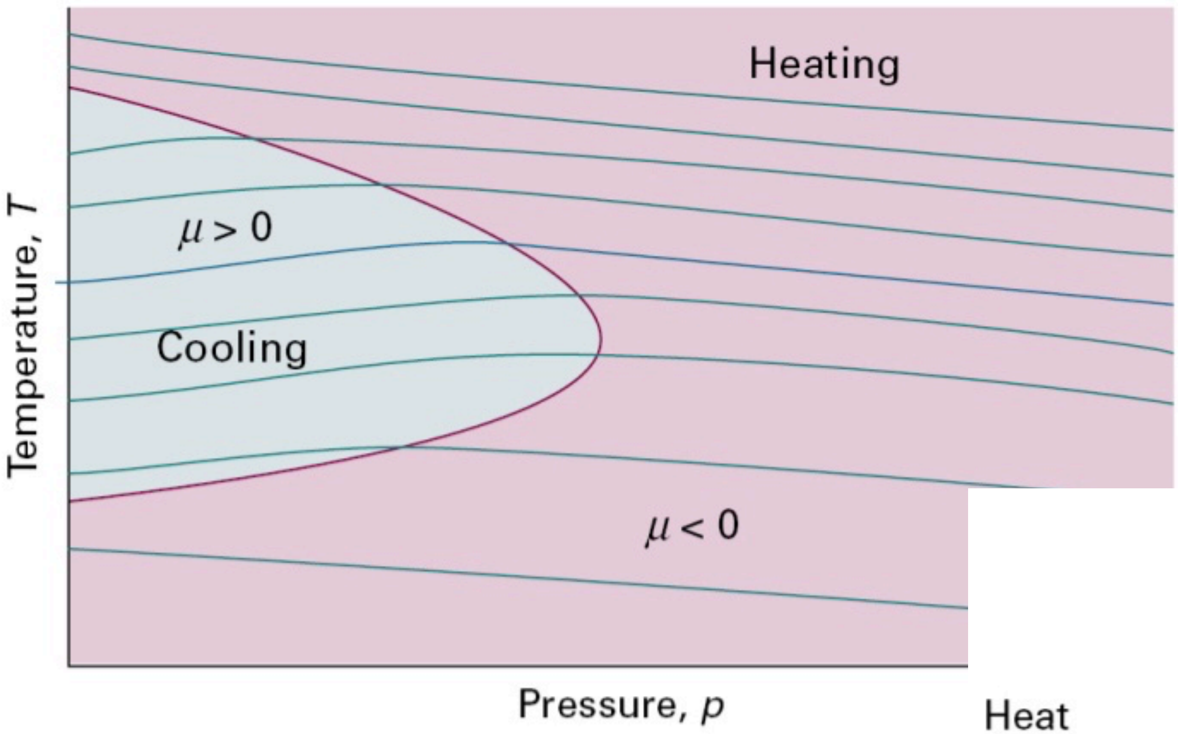
μ is the Joule-Thompson coefficient

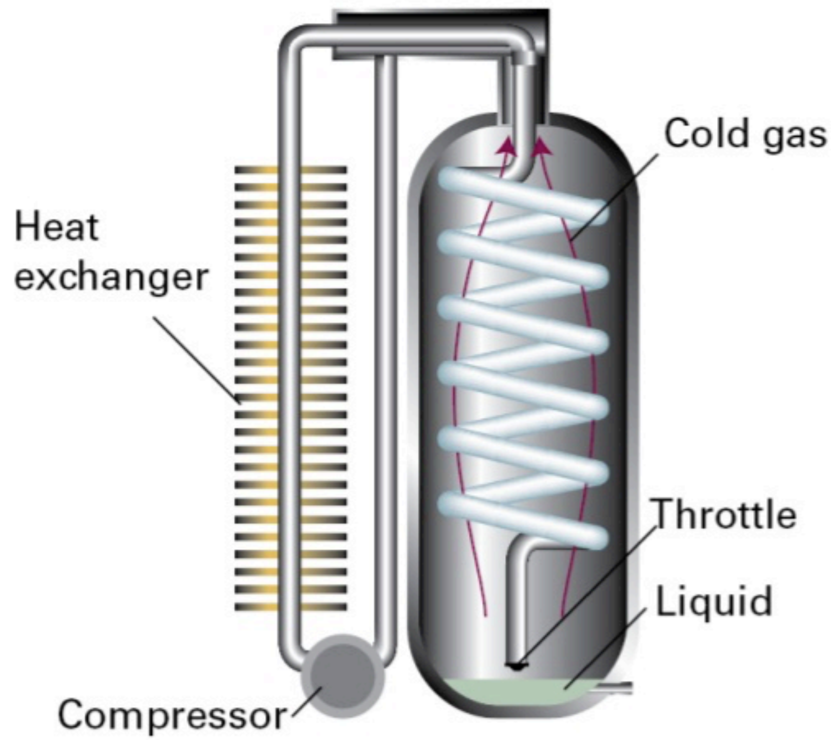
$\mu > 0$ means cooling

Joule-Thompson Experiment

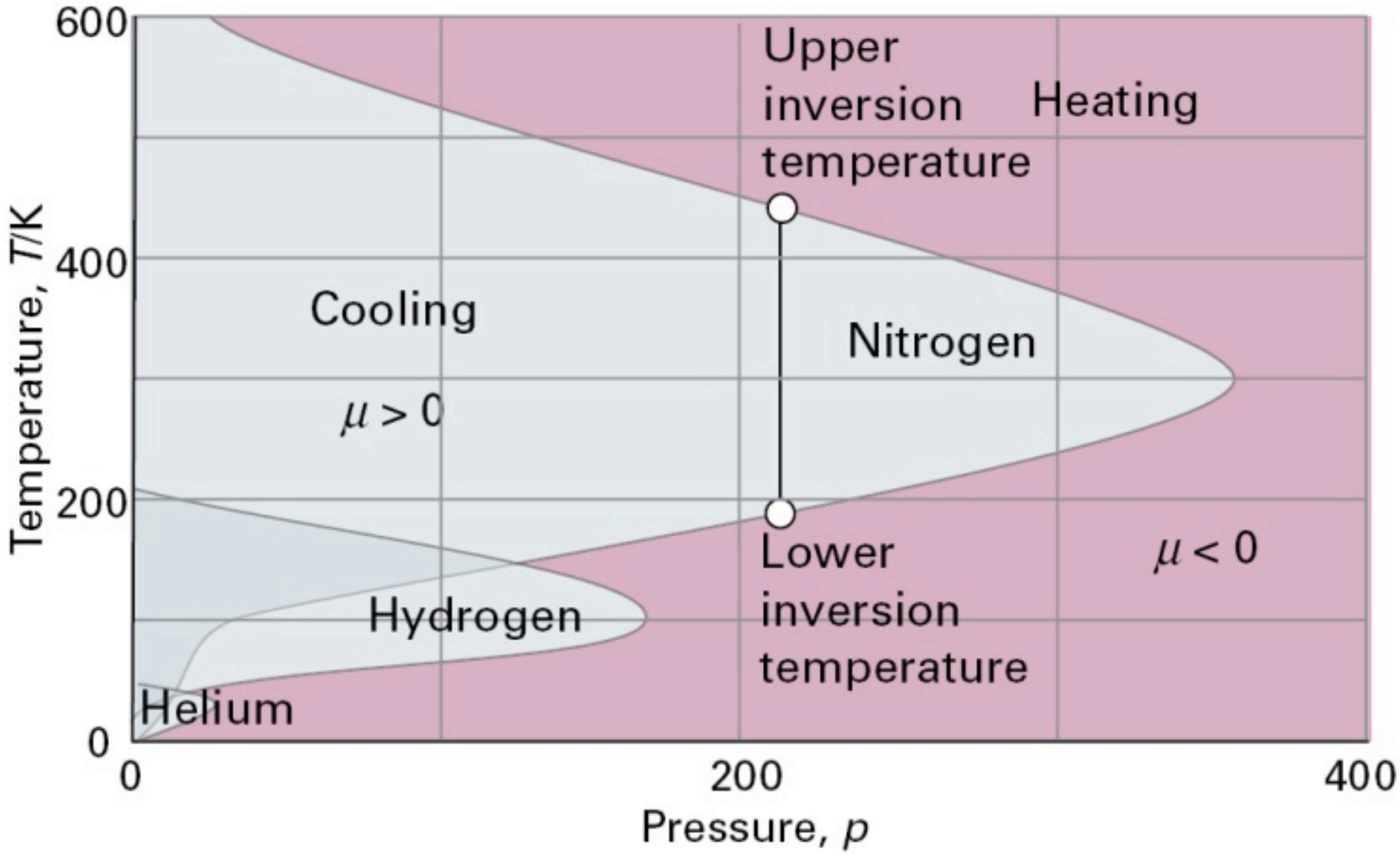


Isenthalpic process: see text: “justification 2D:3, page 96





Use of J-T effect to condense a gas.



Molecular basis of "inversion" temperatures:

$\mu > 0$ attractive interactions are dominant

$\mu < 0$ repulsive interactions are dominant

THE END

SEE YOU Monday