

Physical Chemistry (Chem 132A)



Lecture 10
Wednesday, October 20

New Homework #3 is due October 21

Homework #4 will available October 21 due October 28

Midterm Exam #1, Oct. 25 (Wednesday)



Will cover through Chapter 4

45 minutes

LOGISTICS

- 1. Show up on time**
- 2. Bring Student i.d.**
- 3. There will be a seating chart**
- 4. Bring calculator**

Closed book

**You can bring one 8.5 inch X 11 inch sheet
with hand written equations.**

How does G depend on pressure at constant T?



For an ideal gas: $V_m = RT/p$

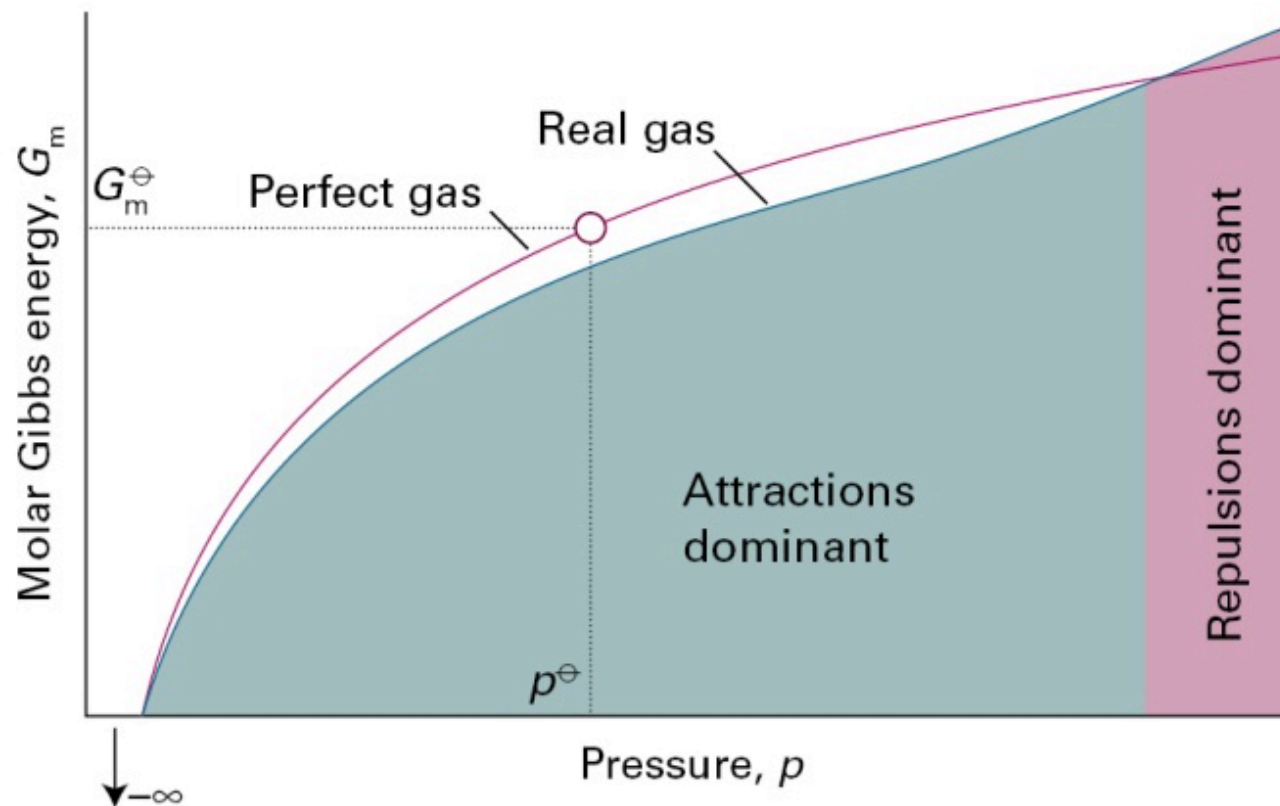
$$G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{1}{p} dp = G_m(p_i) + RT \ln\left(\frac{p_f}{p_i}\right)$$

For a REAL gas: $p = F(V, T)$

$$G_m^0 = G_m^0(p_i) + RT \ln\left(\frac{f}{p^0}\right)$$

Usually take $f = \phi p$

ϕ is called the “fugacity coefficient”





Phase transitions

Consider a phase transition (e.g. melting)

At the normal transition temperature T_{trs}

This means the two phases are in equilibrium.

Equilibrium means the transition is reversible

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

Table 3A.2* The standard enthalpies and entropies of vaporization of liquids at their normal boiling points

	$\Delta_{\text{vap}}H^{\ominus}/(\text{kJ mol}^{-1})$	$\theta_{\text{b}}/^{\circ}\text{C}$	$\Delta_{\text{vap}}S^{\ominus}/(\text{J K}^{-1}\text{mol}^{-1})$
Benzene	30.8	80.1	87.2
Carbon tetrachloride	30	76.7	85.8
Cyclohexane	30.1	80.7	85.1
Hydrogen sulfide	18.7	-60.4	87.9
Methane	8.18	-161.5	73.2
Water	40.7	100.0	109.1

$\Delta_{\text{trs}}S \approx 85 \text{ J K}^{-1}\text{mol}^{-1}$
Trouton's rule.

Chemical Potential (μ)



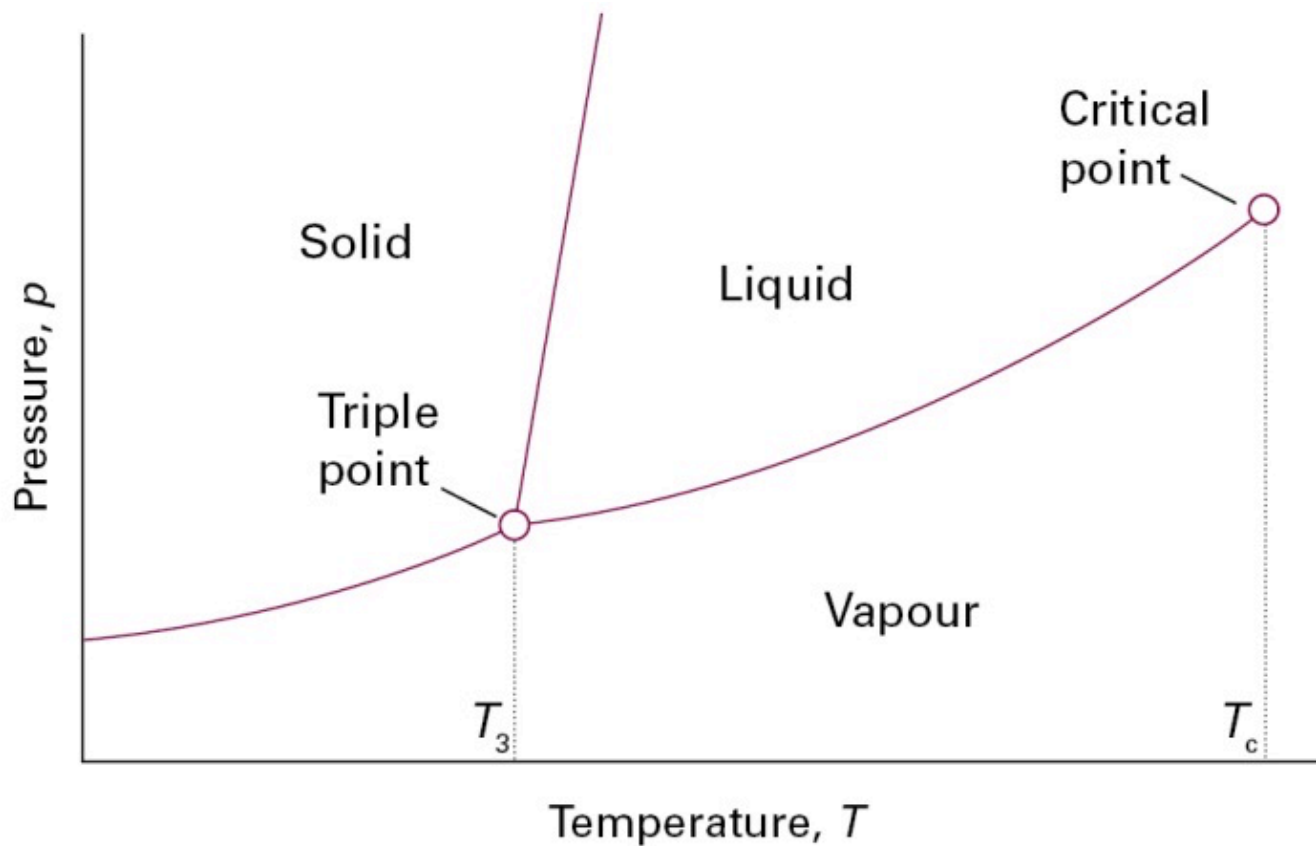
For a single component system $\mu = G_m$

For a system at equilibrium μ is the same everywhere in the sample even if multiple phases are present.

$F = C - P + 2$ The Phase Rule

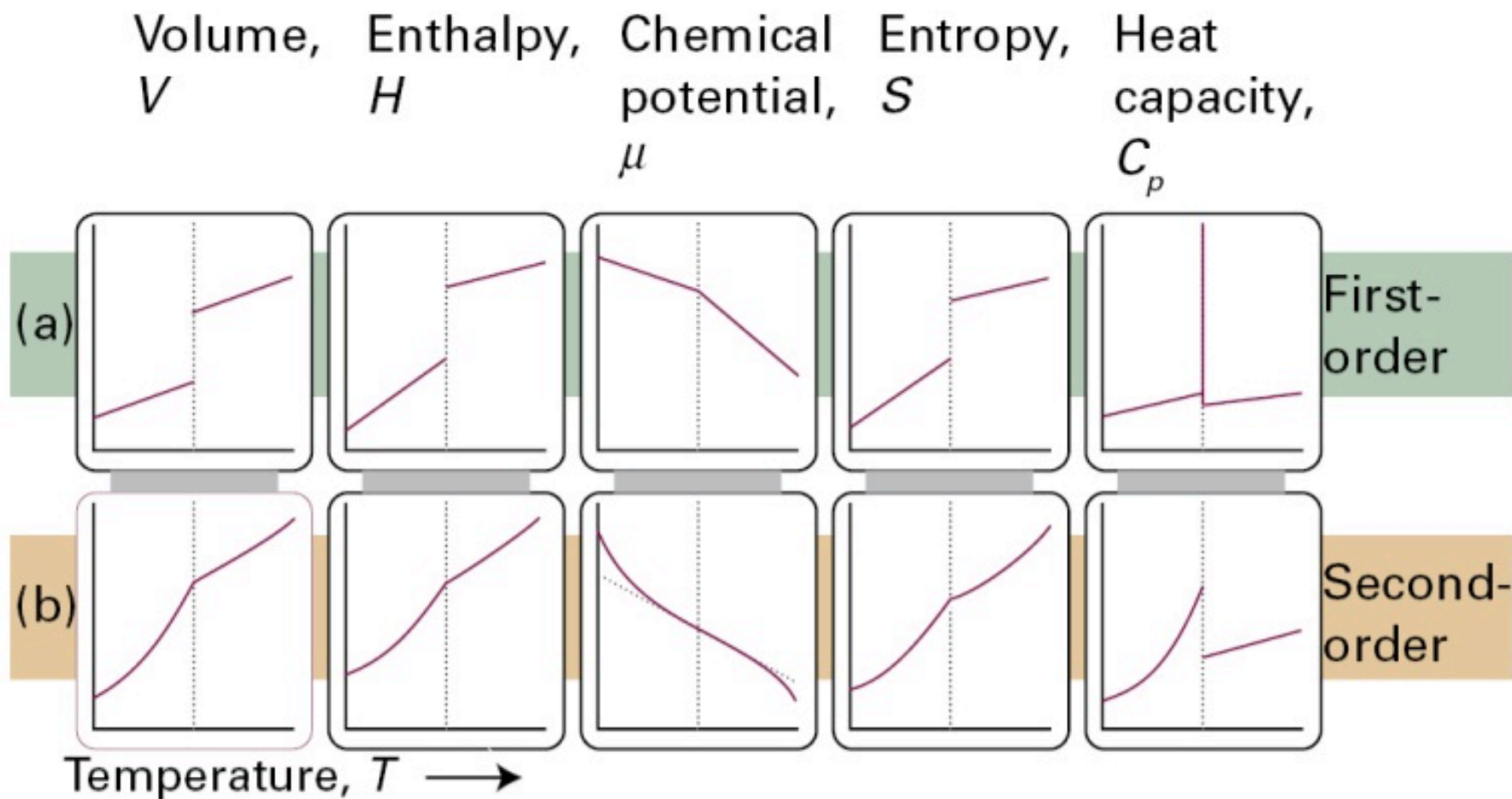


$F = 3 - P$ for single component system





Classification of Phase Transitions



Note: Modern terminology uses “first order transitions” and “continuous transitions”

What happens near a phase transition?

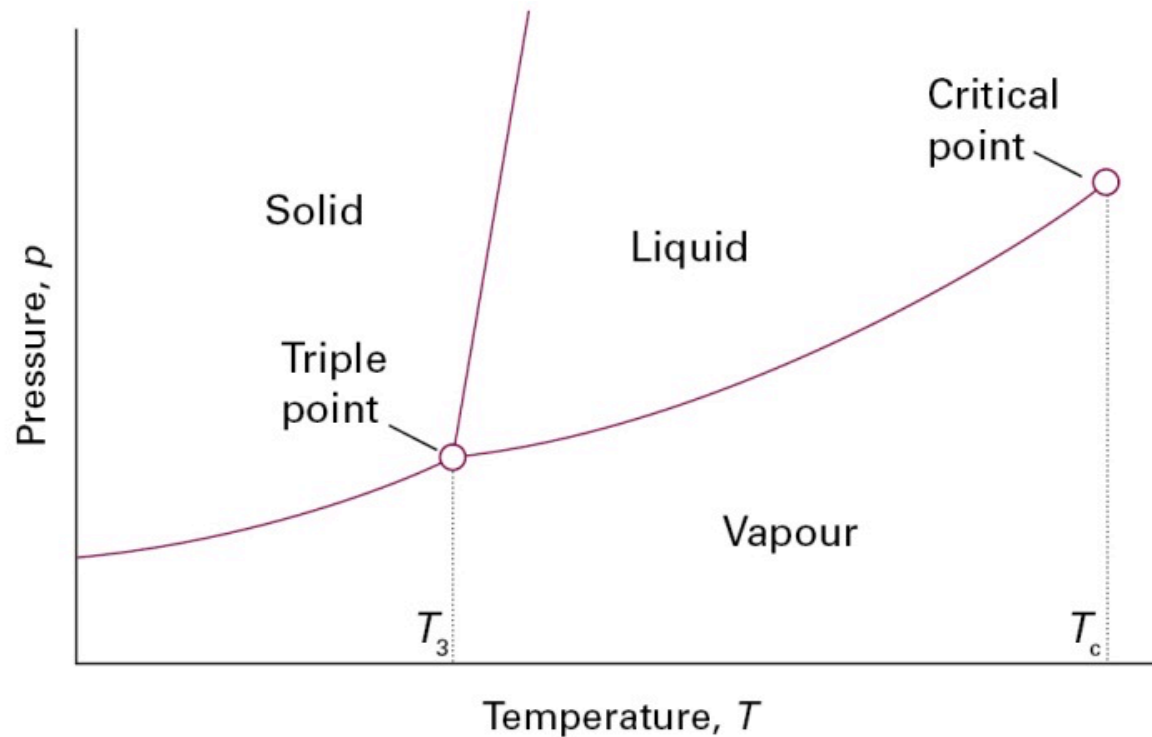


**Consider a single component liquid
near the freezing point.**

Density fluctuations



Phase Boundaries



For example: how does the chemical potential vary with pressure:

$$dG = Vdp - SdT$$

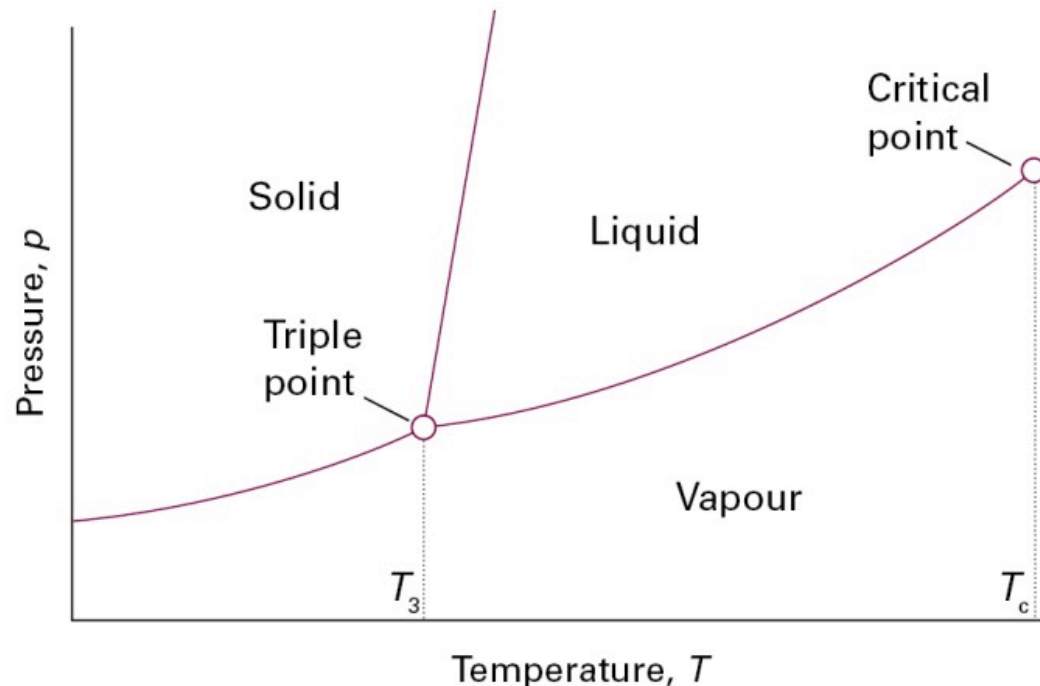
$$\left(\frac{\partial G}{\partial p} \right)_T = V$$

For molar quantities:

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V_m > 0 \quad \text{Usually } V_m(l) > V_m(s) \rightarrow \text{positive slope to solid liquid boundary.}$$

Opposite for water.

Slopes of phase boundaries



On the boundary line the chemical potentials of the two phases are equal:

$$\mu(\alpha) = \mu(\beta)$$

Make a change---to stay on the boundary $d\mu(\alpha) = d\mu(\beta)$

$$d\mu = -S_m dT + V_m dp$$

$$-S_m(\alpha)dT + V_m(\alpha)dp = -S_m(\beta)dT + V_m(\beta)dp$$

$$[S_m(\beta) - S_m(\alpha)]dT = [V_m(\beta) - V_m(\alpha)]dp$$

$$\Delta_{trs} S_m dT = \Delta_{trs} V_m dp$$

$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$

Clapeyron Equation

Specific Case: Liquid/Vapor Boundary



$$\Delta S_{vap} = \left(\frac{\Delta H_{vap}}{T} \right) \quad \text{So we have} \quad \left(\frac{dp}{dT} \right) = \frac{\Delta_{vap} H}{T \Delta_{trs} V}$$

However, $V_m(g) \gg V_m(l)$ so $\Delta_{trs} V = V_m(g) = RT/p$ **for ideal gas**

$$\left(\frac{dp}{dT} \right) = \frac{\Delta_{vap} H}{T(RT/p)} = \frac{p \Delta_{vap} H}{RT^2}$$

$$\frac{d \ln p}{dT} = \frac{\Delta_{vap} H}{RT^2} \quad \text{Clausius-Clapeyron equation}$$

If $\Delta_{vap} H$ is independent of temperature then this can be integrated

$$\int_{\ln p^*}^{\ln p} d \ln p = \frac{\Delta_{vap} H}{R} \int_{T^*}^T \frac{dT}{T^2} = -\frac{\Delta_{vap} H}{RT} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

$$\ln \left(\frac{p}{p^*} \right) = -\frac{\Delta_{vap} H}{RT} \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad \text{Tells how vapor pressure changes with T}$$

For an ideal gas.

This T is a mistake

THE END



SEE YOU FRIDAY