

# Physical Chemistry (Chem 132A)

---



**Lecture 10**  
**Friday, 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.**

# Preparing for the midterm exam



- **Important definitions**

extensive, intensive, state functions, equation of state, closed system, open system, isolated system, reversible, adiabatic, etc.

- **Heat(q) and work(w): sign of w**

- **$\Delta U = q + w$ ,  $dU = dq + dw$**

- **First Law: internal energy of an isolated system is constant**

- **Heat capacity**  $C_V = \left( \frac{\partial U}{\partial T} \right)_V$      $C_p \equiv \left( \frac{\partial H}{\partial T} \right)_p$      $q_v = C_V \Delta T$

- **$H = U + pV$**

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

# Preparing for the midterm exam—page 2



- **Joule-Thompson expansions**

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

- $$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

- **Second Law:** “The Entropy of an isolated system increases in the course of a spontaneous change:  $\Delta S_{total} > 0$ ”

- **for a phase transition:** 
$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$$

- $$\Delta A = \Delta U - T \Delta S$$

**For constant V&T  $\Delta A$  negative is spontaneous**

# Preparing for the midterm exam—page 3



- $\Delta G = \Delta H - T\Delta S$

For constant P&T  $\Delta G$  negative is spontaneous

**Note: quantities are for the SYSTEM**

- Maxwell's relations

- fugacity

- phase boundaries in single component phase diagrams

- phase rule:  $F = 3 - P$  (for single component system)

- definition of 1<sup>st</sup> order and 2<sup>nd</sup> order phase transitions

- $\ln\left(\frac{p}{p^*}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$  **Clausius–Clapeyron Equation**  
**T dependence of vapor pressure**

# MIXTURES



**Start by discussing binary mixtures**

**$x_A + x_B = 1$   $x_i$  = mole fraction of component i.**

**Remember definitions of Molarity (moles/liter) and Molality (moles of solute per kilogram of solvent)**

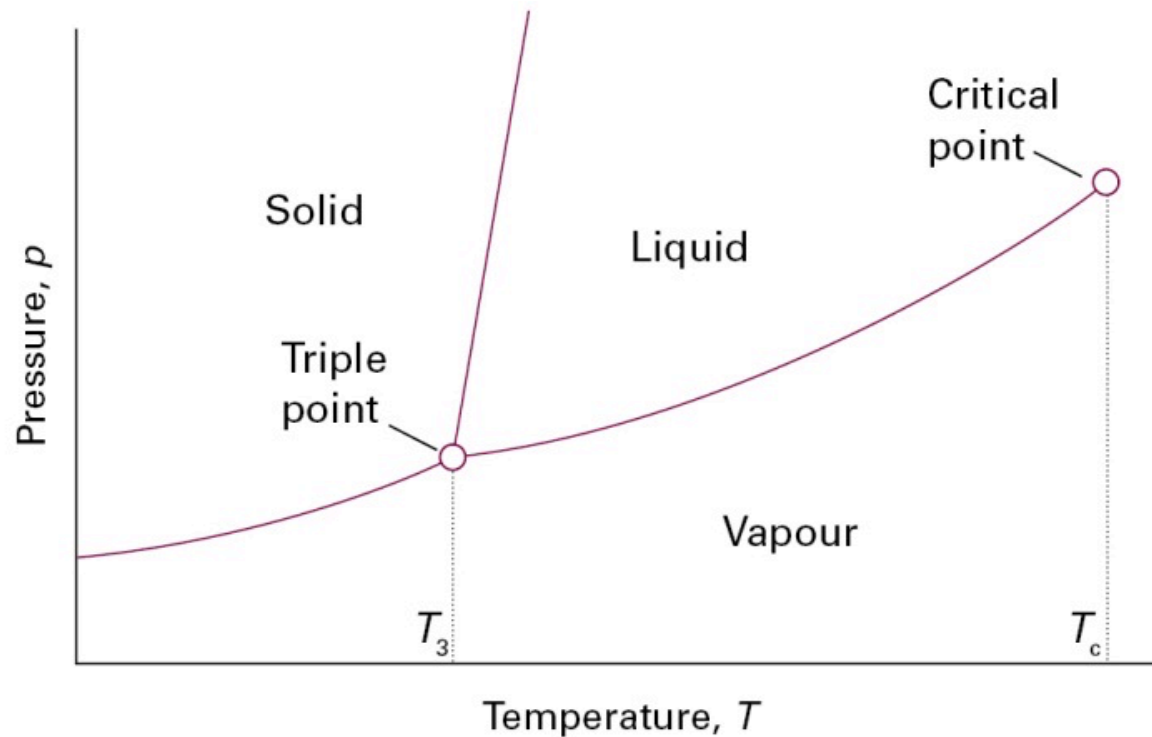
**It is useful to talk about “partial molar quantities”**

**e.g. Partial molar volume**

$$V_j = \left( \frac{\partial V}{\partial n_j} \right)_{p,T,n'}$$



# Phase Boundaries



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

$$dG = Vdp - SdT$$

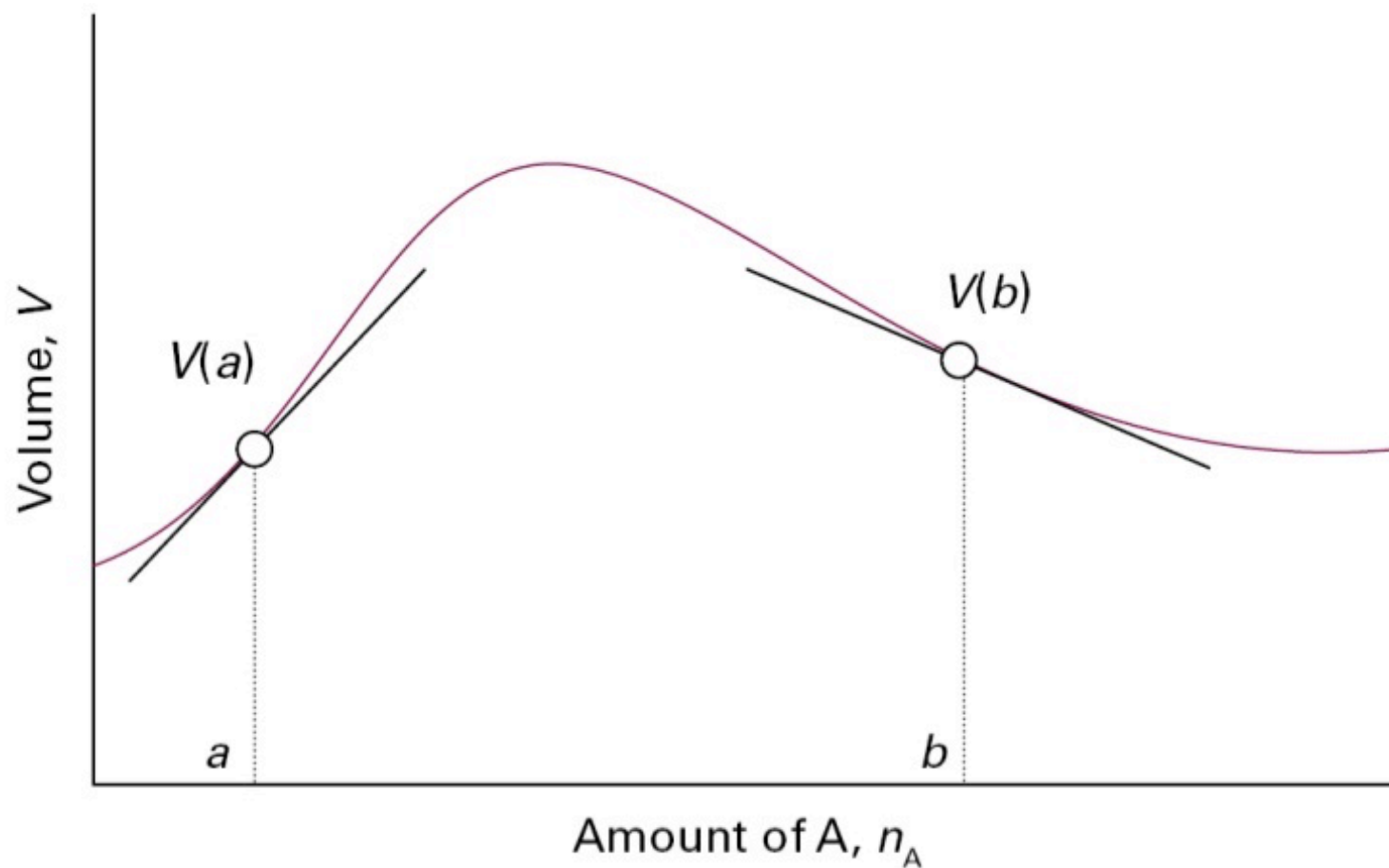
$$\left( \frac{\partial G}{\partial p} \right)_T = V$$

For molar quantities:

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

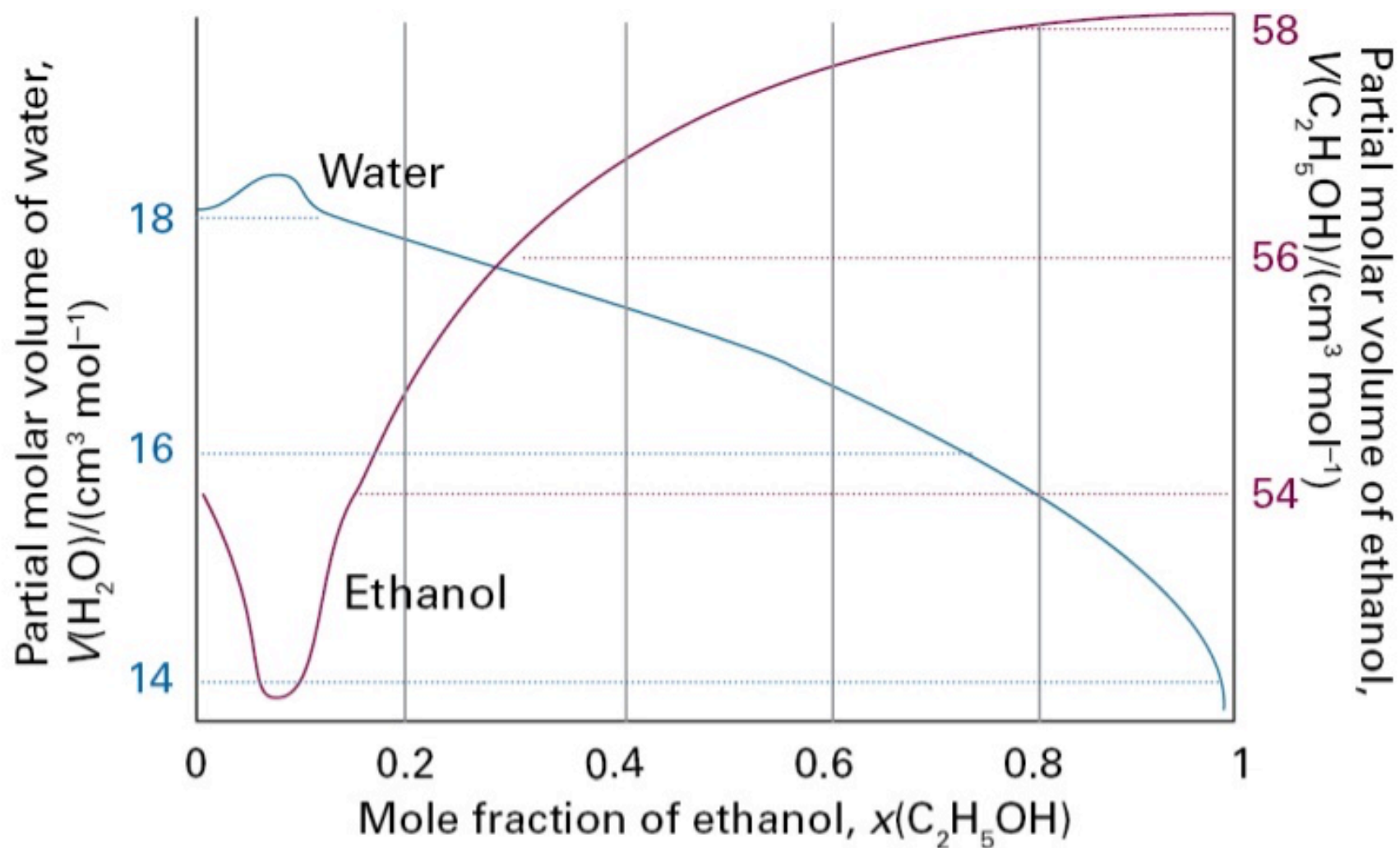
**Opposite for water.**

# Partial molar volume depends on concentration





# Water/Ethanol mixtures (miscible)





$$dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B$$

$$dV = V_A dn_A + V_B dn_B$$

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B$$

## Chemical potential of a component of (j) a mixture $\mu_j$



$$\mu_j \equiv \left( \frac{\partial G}{\partial n_j} \right)_{p,T,n'}$$

Similar to how we wrote the total solution Volume

$$G = n_A \mu_A + n_B \mu_B \quad \text{equation 1}$$

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B$$

So at constant p and T

$$dG = \mu_A dn_A + \mu_B dn_B \quad \text{equation 2}$$

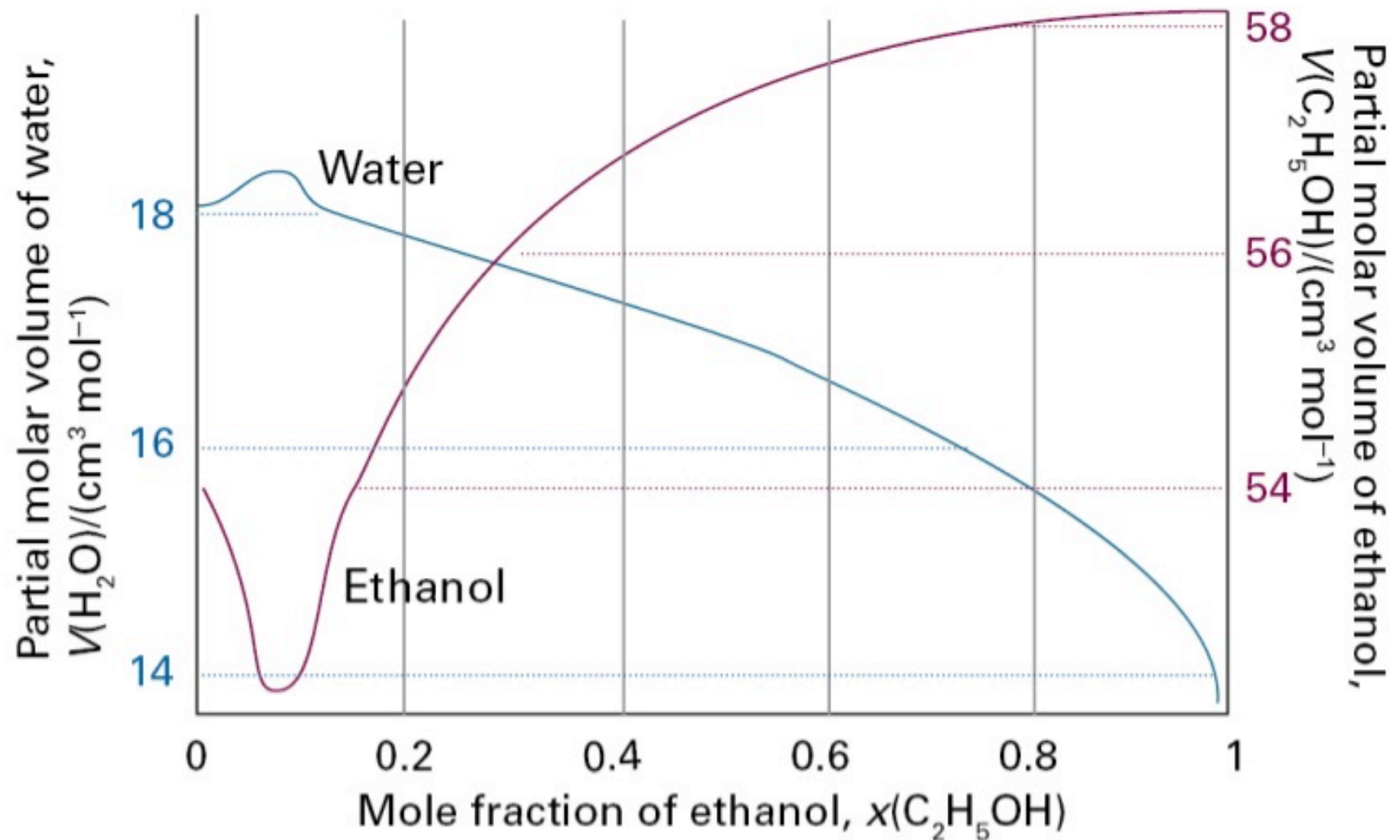
$$\text{from equation 1: } dG = \mu_A dn_A + n_A d\mu_A + \mu_B dn_B + n_B d\mu_B$$

$$\text{Compare equation 1 \& 2 gives: } n_A d\mu_A + n_B d\mu_B = 0$$

Gibbs-Duhem equation.

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Similar argument applies to all partial molar quantities



**THE END**



**SEE YOU MONDAY**