THERMO

- Since you're all gods of thermodynamics and have thoroughly memorized Prausnitz's text, I'll skip over the obvious stuff and get right to a few points you might have thought so obvious as to have totally forgotten.

- Texts

Prausnitz + Smith + Van Ness, of course.
But might I suggest a good physical chem text, say Atkins, or perhaps Alberty? Chemists are kinda dumb, so P-Chem texts explain fundamental concepts in a way that even I can understand.

Basic relations you already KNOW

- Expressions for U, H, G, A
- Maxwell's Relations
- Definitions of Heat Capacity
- Gibb's-Duhem Eqn $(S\partial T - V\partial P + \sum_i n_i d\mu_i = 0)$
- Gibb's-Helmholtz Relation $\left[\dfrac{\partial(G/T)}{\partial(1/T)}\right]_P = H$
- Van der Waals EOS, Virial EOS
- Joule-Thomson Coefficient $\left[\mu_{JT} = \dfrac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P}\right] = \left(\frac{\partial T}{\partial P}\right)_H$
- the three laws of Thermodynamics
- Equilibrium constant in terms of ΔG_f°
- Clapeyron & Clausius - Clapeyron Equations

Generalized Raoult's Law

A Good exercise in keeping track of $\underline{standard\ states}$

a) $\quad f_{iv} = f_{iL}$ $\qquad$ A mixture containing i at some T, P.

b) $\quad \phi_{iv} = \dfrac{f_{iv}}{f_{iv}^0}$ where $f_{v}^0 = y_i P$, so $\boxed{f_{iv} = y_i \phi_{iv} P}$.

c) $\quad \boxed{f_{iL} = x_i \gamma_i f_{iL}^0}$ by definition where f_{iL}^0 is defined at the $T \& \underline{\underline{P}}$ of the solution

f_{iL}^0 is typically taken as the fugacity of the pure liquid i at the T, P of the solution. (In dilute soln, use Henry's Law)
$$\text{so} \quad \boxed{f_{iL}^0 = f_{iL}^{pure}}$$

d) what is f_{iL}^{pure}? we know that $f_{i\,pure}^{L} = f_{i\,pure}^{V}$
But this is true at the saturation pressure of the pure liquid. (not the mixture pressure)

However, we need $f_{i\,pure}^{L}$ at the mixture pressure.

So, use the Poynting correction
$$\boxed{f_{i\,pure}^{L\,P_{soln}} = f_{i\,pure}^{L\,P^{sat}} \left[\int_{P_i^{sat}}^{P^{soln}} exp\left(\dfrac{v_i^L}{RT}\right) dP \right]}$$

e) But $f_{i\,pure}^{V\,P_{sat}} = \phi_i^{P_{sat}} P^{sat} = f_{i\,pure}^{L\,P_{sat}}$

$$\text{So} \quad \boxed{f_{iL}^0 = \phi_i^{P_{sat}} P^{sat} (PC)} \quad (\gamma_i = 1 \text{ because pure component})$$

f) So finally
$$\boxed{y_i \phi_{iv} P = x_i \gamma_i \phi_i^{P_{sat}} P^{sat} (PC)}$$

what is the phase diagram of water?
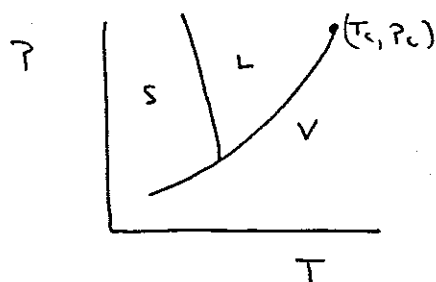
a) where is the critical pt?

b) why does the S-L curve have a negative slope?

Realize that beyond the critical point there is no longer a distinction between vapor & liquid.

At a phase transition (at least a typical phase transition) the Gibbs Free energy is the only state variable that remains continuous. Phase transitions are characterized by infinite heat capacity at the transition temperature.

L-V, S-V & S-L transitions are all characterized by the equating of chemical potentials $\mu^\alpha = \mu^\beta$

at a phase transition at a given T, P

$$\mu^\alpha = \mu^\beta$$

$$G = E - TS + PV$$

If one follows the equilibrium curve

$$\partial\mu^\alpha = \partial\mu^\beta \qquad \text{But } d\mu_i = V\partial P - S\partial T$$

So

$$V^\alpha \partial P - S^\alpha \partial T = V^\beta \partial P - S^\beta \partial T$$

So $$\boxed{\frac{\partial P}{\partial T} = \frac{S^\alpha - S^\beta}{V^\alpha - V^\beta}}$$ which is the Clapeyron eqⁿ

appropriate simplification yields the Clausius–Clapeyron Eqⁿ (for V-L equilibria

$$\left(\begin{array}{c}\text{derived on}\\\text{next page}\end{array}\right) \qquad \boxed{\frac{\partial \ln P}{\partial T} = \frac{\Delta H vap}{RT^2}}$$

(having assumed neglisible molar volume of the liquid and an ideal gas

Just an interesting point: The above equation, upon integration and substitution of a B.C. (either the triple point or the critical point), yields an approximate equation for the curves on the phase diagram above.

Derivation of Clausius Clapeyron Eqn:

$$\frac{\partial P}{\partial T} = \frac{\Delta S}{\Delta V}$$

since phase transition occurs at a constant T

$$\Delta S = \frac{\Delta H}{T} \longrightarrow$$

$\Delta G = \Delta H - T\Delta S$ At phase transition

$\Delta H = T\Delta S$; $\Delta S = \frac{\Delta H}{T}$ $\Delta G = 0$

so $\frac{\partial P}{\partial t} = \frac{\Delta H}{\Delta V(T)} = \frac{\Delta H_{vap}}{[V_{gas} - \cancel{V_{liq}}(T_b)]}$ for vapor-liquid transition

Small!

let $V = \frac{RT}{P}$ for gas phase.

$$\frac{\partial P}{\partial T} = \frac{\Delta H_{vap}\, P}{R T_b^2} \qquad , \qquad \frac{\left(\frac{\partial P}{P}\right)}{\partial T} = \frac{\Delta H_{vap}}{R T_b^2}$$

or, equivalently

$$\boxed{\frac{\partial \ln P}{\partial T} = \frac{\Delta H_{vap}}{R T_b^2}} \longrightarrow \text{Clausius – Clapeyron Eqn}$$

The Critical Point:

Taking V-d Waals EOS
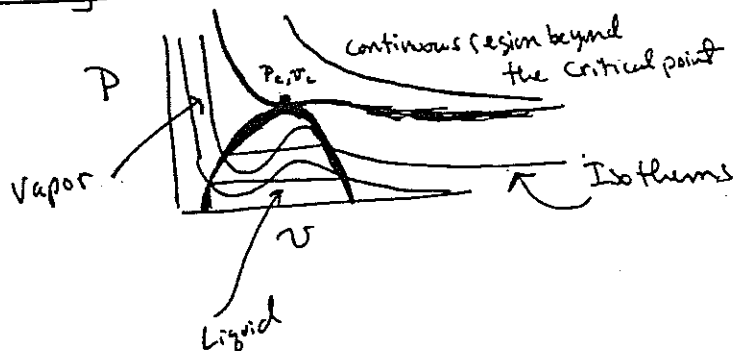
The critical point occurs where

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$$
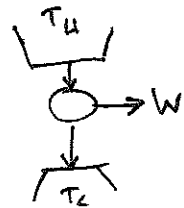
(inflection point)

The Carnot Cycle

P

V
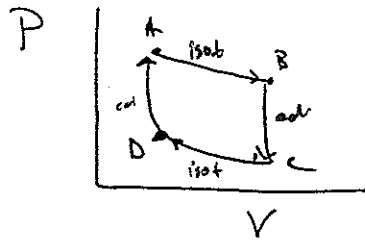
$A \to B$ isothermal expansion Q_{in}

$B \to C$ adiabatic expansion $Q = 0$

$C \to D$ isothermal compression Q_{out}

$D \to A$ Adiabatic compression $Q = 0$

now $\Delta U = 0$ So

$$W = Q = Q_{in} - Q_{out}$$

(work done by system is positive

Q entering system is positive)

$$e = \frac{\text{Work out}}{\text{Heat in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \boxed{1 - \frac{Q_{out}}{Q_{in}} = e}$$

T_H
→ W
T_C

What is $\dfrac{Q_{out}}{Q_{in}}$?

$$Q_{in} = Q_{AB} = W_{AB} = RT_h \ln \frac{V_B}{V_A}$$

(because isothermal $\Delta U = 0$)

Similarly

$$Q_{out} = Q_{CD} = W_{CB} = RT_C \ln \frac{V_C}{V_D}$$

So $\dfrac{Q_{out}}{Q_{in}} = \dfrac{T_C \ln(V_C/V_D)}{T_h \ln(V_B/V_A)}$

since $PV = RT$

$$TV^{\gamma-1} = \text{constant}$$

applying to $B \to C$

$$T_h V_B^{\gamma-1} = T_C V_C^{\gamma-1}$$

$$T_h V_A^{\gamma-1} = T_C V_D^{\gamma-1}$$

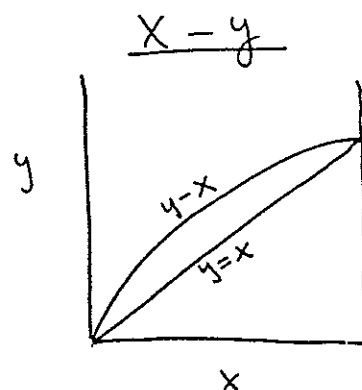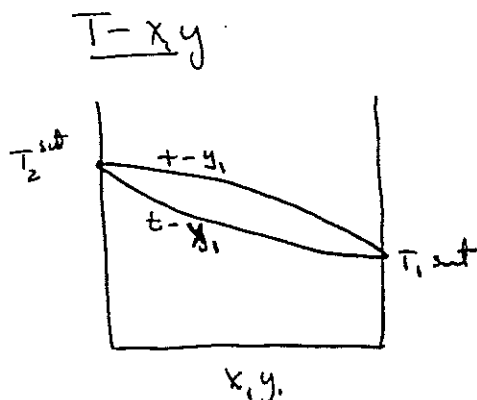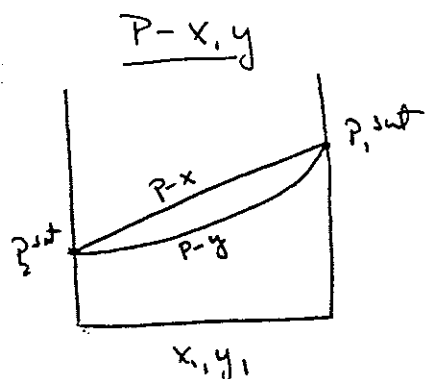or $\left(\dfrac{V_B}{V_A}\right)^{\gamma-1} = \left(\dfrac{V_C}{V_D}\right)^{\gamma-1}$

$$\boxed{\frac{V_B}{V_A} = \frac{V_C}{V_D}}$$

it can be shown that

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

by recalling that

$$PV^{\gamma} = \text{constant for any}$$

quasi-static adiabatic process
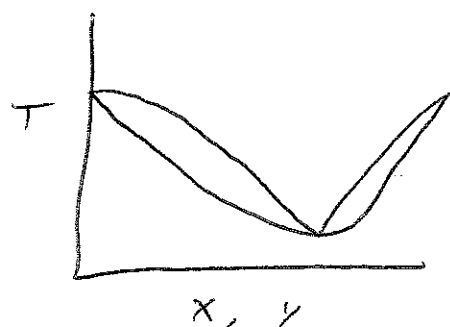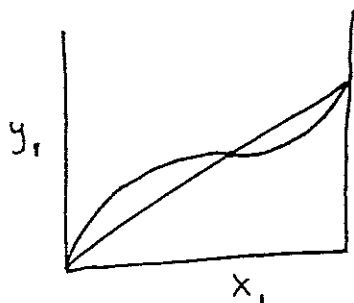
So $\dfrac{Q_{out}}{Q_{in}} = \dfrac{T_C}{T_h}$

$$\boxed{e = 1 - \frac{T_C}{T_h}}$$

V-L Phase Diagrams

Ideal

P-X,y

T-Xy

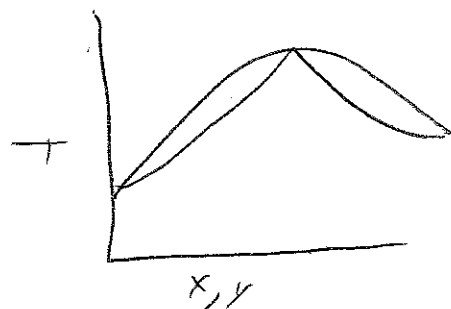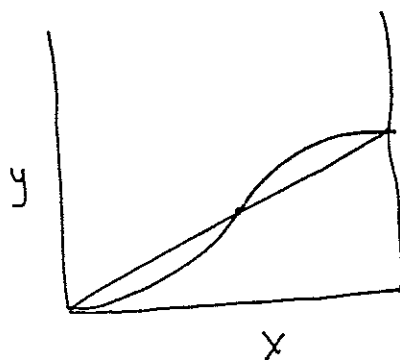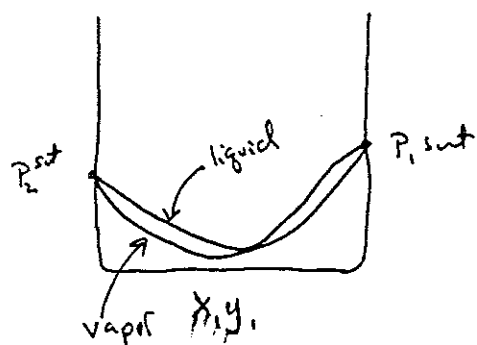### X-y

Positive deviations from Raoult's Law w/ azeotrope

MIN BP, HIGH P AZEOTROPE
$P_1^{sat} > P_2^{sat}$
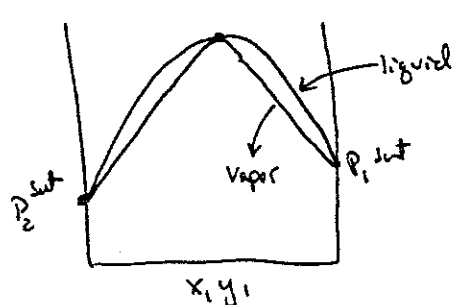
Negative deviations from Raoult's Law w/ low boiling azeotrope

pressure — MAX BP

At moderate pressure non-idealities are always due to liquid phase activity coefficients, as vapor phase fugacity coefficients are very near unity.

from Raoult's Law

Positive deviations imply activity coefficients > 1. g^E is consequently > 0

negative deviations from R.L imply $\gamma < 1$ $\quad g^E < 0$

Is there a relation between azeotrope formation and the behavior of the excess Gibbs Free energy?

$$\ln \gamma = \frac{\overline{G_i^E}}{RT} = \left[\frac{\partial n G_i^E / RT}{\partial n_i} \right]_{P, T, n_j}$$

Miscibility

In typical phase diagrams, we have two degrees of Freedom. We can set x_1, P and then T is specified for example.
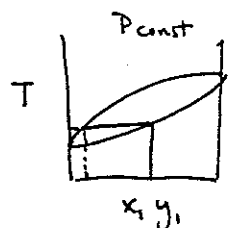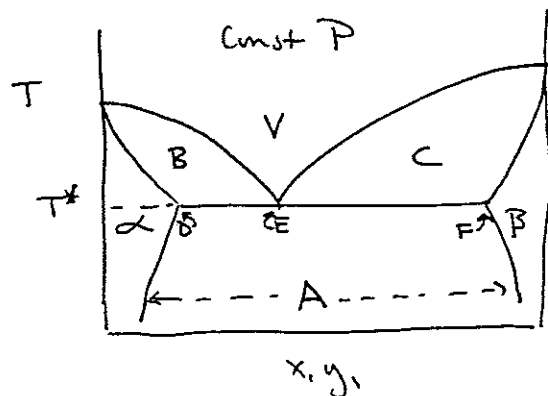
This follows from the Gibbs Phase rule

$$\boxed{F = m + 2 - \pi}$$

- # of degrees of freedom
- # of components
- # of phases

So for 2 component, 2 phase

$$F = 2 + 2 - 2 = 2 \text{ degrees of freedom}$$

Now take a 2 component system whose phase diagram at a given P is the following

Here two liquid phases, α, β + one vapor phase are possible

In region A, $\alpha - \beta$ exist in equilibrium, use the lever rule to find the relative proportions of each.

In B, $\alpha - V$ equilibrium

In C, $\beta - V$ equilibrium

At Temperature T^*, all three phases are present. Using the Phase rule realize that $F = 2 + 2 - 3 = 1$ degree of freedom which is the Pressure specified to write the diagram. Thus the compositions of α, β, V are all specified. The relative proportions are specified by the lever rule.

Critical Solution temperatures
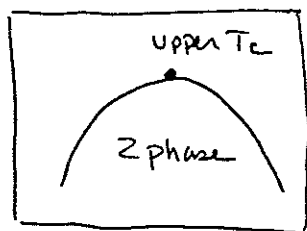
At a sufficiently high temperature, A-B interactions + thermal energy are sufficient to break A-A, B-B interactions (Lewis acid-base, H-bonding) and form one phase.
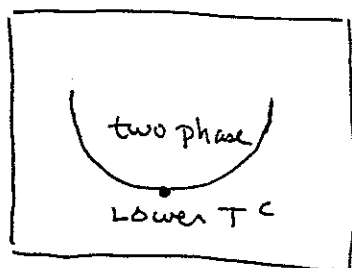
Relatively rare. Aqueous mixtures of amines are an example. At low temperatures A-B H-bonding may occur, but at higher temperatures, thermal interactions are sufficient to break these bonds.

Remember that $\Delta G_{mixing} > 0$ (not Δg^E)
will precipitate pure component phase separation
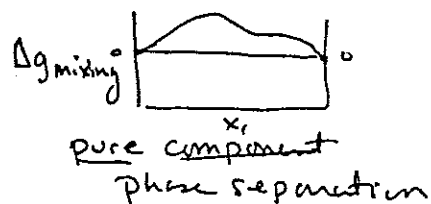
But that any downward concavity in the Δg_{mixing} curve will cause some sort of phase separation, although not back to pure component compositions.
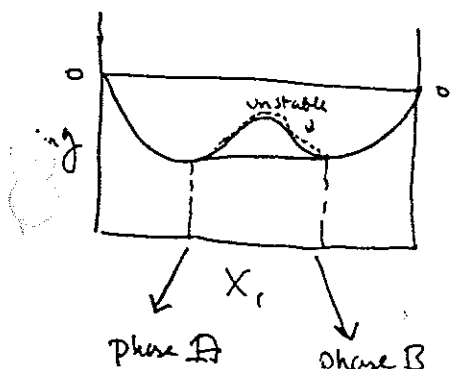
Phase A + Phase B result in a lower Δg_{mixing} than a single phase in the unstable region

So a negative Δg_{mixing} does not guarantee phase miscibility.