Test 2

CHBE 3130 A **Thermodynamics II**

Instructor: Dr. Carson Meredith Fall 2013

Instructions: Write your final answers in the boxed areas on each question. Show your work below the boxed answers.

Name: ____________________________________

Honor Statement:

I commit to uphold the ideals of honor and integrity by refusing to betray the trust bestowed upon me as a member of the Georgia Tech community.

Signature: ______________________________________

1) At 5 °C two immiscible liquid phases, α and β, are in equilibrium. Phase α makes up 40 mol% of the total system (phases $\alpha + \beta$) and consists of pure component (1). The remainder is phase β, which consists of pure component (2). The two liquids are slowly heated at constant pressure, P, and a vapor phase appears at T = 35 °C, in equilibrium with the two liquids.

The Antoine coefficients are

Component	A	B	C
1	15.5	3900	270
2	16.0	3600	280

$$\ln(P) = A - B / (T + C)$$, where P is in [kPa] and T is in [°C]

(a) 7 pts. Find the system pressure, P, and the composition of the vapor that forms at 35 °C (y_1^*)

$P_1^*(35\ °C) = 15.08$ kPa

$P_2^*(35\ °C) = 96.68$ kPa

$P = P_1^* + P_2^* = 111.8$ kPa

$y_1^* = P_1^*/P = 0.135$

(b) 7 pts. If you continue to heat beyond 35 °C at constant P, at what temperature, T, will the last drop of liquid become vapor?

Original overall composition of component 1 is $z_1 = 0.4$.

Hence, when it all becomes vapor the $y_1 = z_1 = 0.4$.

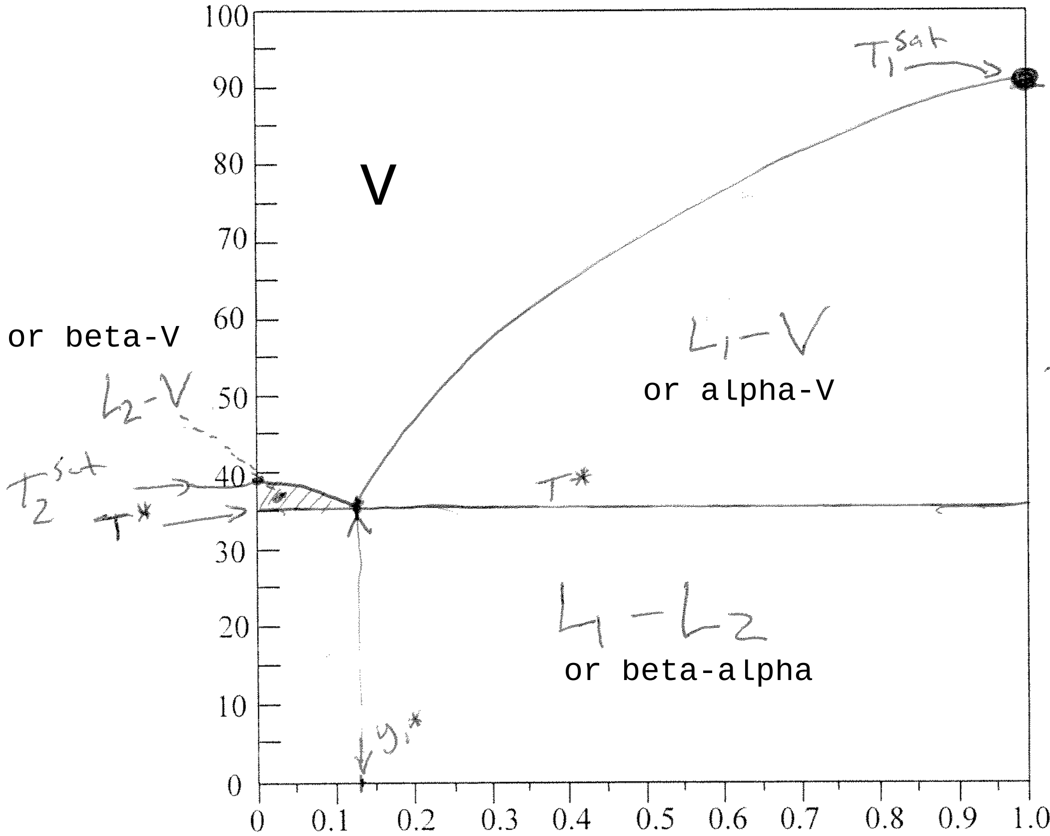
$y_1P = P_1^* = 0.4(111.8) = 44.7$ kPa

$\ln(P_1^*) = 44.7 = 15.5 - 3900 / (T + 290)$

$T = 63.35$ °C

(c) 7 pts.

Draw a sketch of the T vs. x_1, y_1 phase diagram for <u>the system described *in this problem*</u>. The diagram should correctly show the location of the essential <u>points</u> where phase boundaries (e.g., coexistence curves or lines) intersect one another or intersect an axis. The coexistence <u>curves/lines</u> themselves *don't have to be numerically exact* but should *represent the expected shape*. Label the points and label the types of phases present in each bounded region. See example below.



$P = 111.76$

find:

$T_1^{sat} = -C_1 - \frac{B_1}{\ln(P) - A_1}$

$T_1^{sat} = 91.66\ °C$

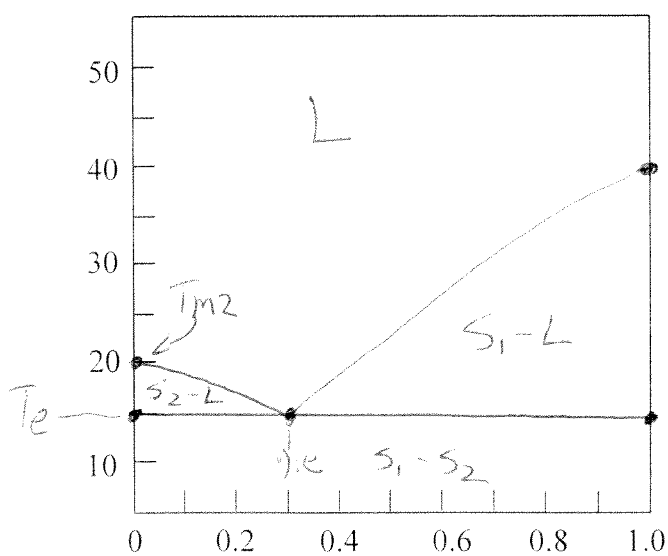
$T_2^{sat} = -C_2 - \frac{B_2}{\ln(P) - A_2}$

$T_2^{sat} = 39.1\ °C$

Example:

If, for example, this were SLE with $T_{m1}=40$, $T_{m2}=20$, $T_e=15$ and $y_{1e}=0.3$

The diagram should have points, lines, and labels like this:



(2) At T = 60 °C the vapor pressure of one component in a binary mixture is $P_1^* = 1.5$ bar, and the vapor pressure of component 2 is $P_2^* = 0.9$ bar. The partial-molar excess Gibbs energy can be described by

$$\frac{G^E}{RT} = Ax_1x_2,$$

where A = 1.9, x_i is liquid mole fraction, R = gas constant, and T = temperature.

(a) 7 pts. Is it possible for a liquid mixture of 1 and 2 to phase separate into two phases (LLE)? Why or why not?

No, because A < 2.

Alternatively you can show that ΔG_{mixing} is always < 0.

$\Delta G_{mixing} = G - \sum x_iG_i$

$G^E = G - \sum x_iG_i - RT\sum x_i\ln(x_i) \rightarrow G = G^E + \sum x_iG_i + RT\sum x_i\ln(x_i)$

Thus $\Delta G_{mixing} = G^E + \sum x_iG_i + RT\sum x_i\ln(x_i) - \sum x_iG_i$

$\Delta G_{mixing}/RT = G^E/RT + (x_1\ln x_1 + x_2\ln x_2) = Ax_1x_2 + (x_1\ln x_1 + x_2\ln x_2)$

It is easy to show that even for the lowest value of x_1 and $x_2=1-x_1$ that Ax_1x_2 is always positive and it's magnitude is always less than $(x_1\ln x_1 + x_2\ln x_2)$, which is always negative.

(b) 7 pts. At 60 °C, a liquid with a composition of $x_1=0.5$ is in equilibrium with a vapor of unknown composition. Calculate the pressure, P, and the vapor composition, y_1. State all assumptions.

Because pressure is low, assume ideal gas and ignore Poynting factor. Cannot assume ideal solution because A ≠ 0 and therefore $G^E \neq 0$.

Write two fugacity equalities.

$y_1P = x_1\gamma_1P_1^*$

$y_2P = x_2\gamma_2P_2^*$

add: $P = x_1\gamma_1P_1 + x_2\gamma_2P_2^*$

$\gamma_1 = \exp(A(x_2)^2) = \exp(1.9(0.5)^2) = 1.608$

$\gamma_2 = \exp(A(x_1)^2) = \exp(1.9(0.5)^2) = 1.608$

$P = 0.5(1.5)(1.608) + 0.5(0.9)(1.608) = 1.93$ bar

$y_1 = x_1\gamma_1P_1^*/P = 0.625$