

Test 1

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: SOLUTION

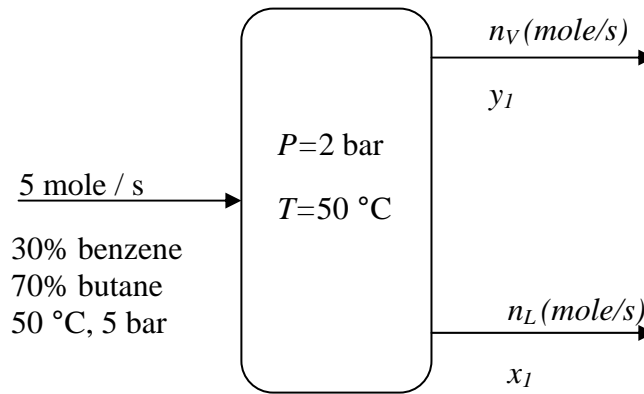
Honor Statement:

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) The phase diagram for benzene (1) and butane (2) at 50 °C is given on the next page.

- (a) 10 points : In the process below, what are the compositions of benzene in the liquid and vapor phases (x_1 and y_1) and what are the flowrates of liquid and vapor (n_L and n_V) out of the vessel at steady state?



Write answers : $x_1 = 0.64$ $y_1 = 0.12$ $n_L = 1.73$ (mole/s) $n_V = 3.27$ (mole/s)

Show work here or on next page:

This is a flash calculation at 50 °C and 2 bar, with initial composition of $z_1=0.3$. Read off $P = 2$ bar and $z_1=0.3$ to find the intersection with the bubble and dew-point curves. From the bubble point curve, $x_1 = 0.64$ and from the dew point curve, $y_1 = 0.12$.

The lever rule (or mole balance) yields vapor fraction V

$$V = (x_1 - z_1) / (x_1 - y_1) = (0.64 - 0.3) / (0.64 - 0.12) = 0.654$$

$$n_V = 0.654 \times 5 \text{ mole/s} = 3.27 \text{ mole/s}$$

$$n_L = 5 - n_V = 1.73 \text{ mole/s}$$

Alternative solution: Read $P_1^{sat} = 0.6$ and $P_2^{sat} = 4.9$ bar from chart, and use Raoult's law to calculate x_1 and y_1 , then mole balance to get n_L and n_V .

- (b) 5 points: Does this system behave as an ideal mixture? Why or why not?

Answer 1. The vapor phase is ideal because the pressure is low enough to be considered an ideal gas, and an ideal gas is always an ideal mixture. The answer for the liquid phase must contain a reference to their chemical similarity. Two answers were acceptable:

- i. The molecules are chemically similar because they are hydrocarbons and will behave nearly ideally. (this is the minimum I was looking for – something about molecule similarity → ideal mixing)
- ii. The molecules, while hydrocarbons, are different chemically and structurally. Benzene is an aromatic and butane is an alkane and the C-C bonds are different.

Benzene is a stiff, planar ring and butane is a flexible 'chain' with possibility of rearranging into different conformers. Hence, some non-ideality can be expected.

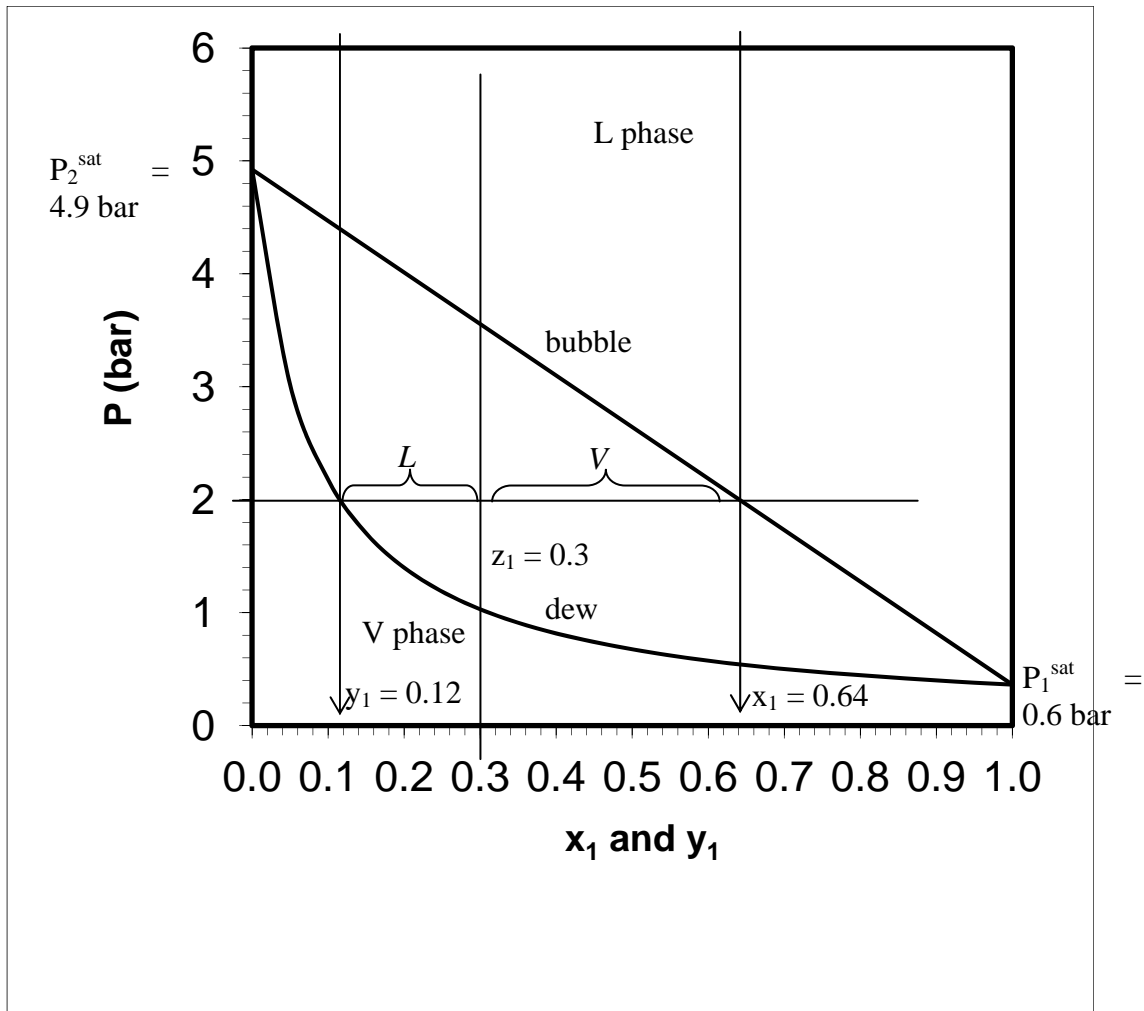
In reality this system would be close to ideal, but not exactly ideal.

2. Another type of answer that was acceptable is that the linear bubble line on the phase diagram indicates that Raoult's law is followed, therefore they are ideal mixtures.

Some wrong answers: The ideality has nothing to do with temperature. If anything, solutions become less ideal as T is lowered, and more ideal as T is increased. But 50 C is not an unusually high or low T .

The ideality has nothing to do with the vapor or liquid flow rates or the interactions *between* the vapor and liquid phases.

Some students wrote that because they are similar the molecules would be non-interacting. Only an ideal gas is non-interacting. An ideal solution or mixture contains 'real' molecules that have real interactions. The interactions are balanced, however, leading to purely randomized mixing of components, e.g., no preference for one component interacting with any other component.



2) 10 points: Two substances, an acid (1) and water (2), are mixed together and evolve heat during their mixing (exothermic). If the mixing occurs isothermally, and the evolved heat is measured to be $Q = -65$ kJ, and the total number of moles is $n = 10$ moles, how many moles of acid were added, n_1 ?

Information available: $H_1 = -50$ kJ/mole $\bar{H}_1 = -55$ kJ/mole
 $H_2 = -30$ kJ/mole $\bar{H}_2 = -37.5$ kJ/mole

Write answer : $n_1 = 4$ moles

Show work :

$$Q = H^E$$

The heat given off is a result of going from the initial (unmixed, pure) state to the final (mixed) state. The enthalpy change is enthalpy of mixture minus enthalpy of pure components.

$$Q = \Delta H = H^t - H_1^t - H_2^t$$

Some students recognized that $Q = H^E$, which is also true and equal to the difference above.

$$H_1^t = n_1 H_1$$

$$H_2^t = n_2 H_2$$

$$H^t = n(H) = n_1 \bar{H}_1 + n_2 \bar{H}_2$$

$$Q = n_1 \bar{H}_1 + (n - n_1) \bar{H}_2 - n_1 H_1 - (n - n_1) H_2$$

$$-65 \text{ kJ} = n_1 (-55 + 50) + (10 - n_1)(-37.5 + 30) \text{ kJ}$$

$$-65 = n_1 (-55 + 50) + (10 - n_1)(-37.5 + 30) = 10(-7.5) + (7.5 - 5) n_1$$

$$n_1 = (-65 + 75) / (2.5) = 4 \text{ moles}$$

- 3) 10 points: The free energy change, $G_2 - G_1$, for compressing a pure gas from $P_1 = 10$ bar to $P_2 = 20$ bar is 1,466 J/mole. What is the 2nd virial coefficient of the gas, B , in cm^3/mol ? The compression is carried out at a constant temperature of 300 K.

Write answer : $B = -263 \text{ cm}^3/\text{mol}$

Show work :

Recall that $\mu_i = G_i$ for a pure gas.

$$G_i = I_i + RT \ln(f_i)$$

Thus,

$$G_2 = I_2 + RT \ln(f_2)$$

$$- \quad G_1 = I_1 + RT \ln(f_1)$$

$$G_2 - G_1 = RT \ln(f_2) - RT \ln(f_1)$$

I_1 and I_2 are temperature dependent constants, and they are equal since $T = \text{constant}$. Thus, they cancel in the subtraction above.

$$(G_2 - G_1)/RT = \ln(f_2/f_1) = \ln(\phi_2/\phi_1 * P_2/P_1) = \ln(\phi_2/\phi_1) + \ln(P_2/P_1)$$

$$\ln(\phi_2/\phi_1) = (G_2 - G_1)/RT - \ln(P_2/P_1)$$

$$\ln(\phi_i) = B_i P_i / RT_i$$

$$\ln(\phi_2/\phi_1) = B_2 P_2 / RT_2 - B_1 P_1 / RT_1$$

Note that B is dependent only on temperature. Thus, $B = B_1 = B_2$ and

$$\ln(\phi_2/\phi_1) = B(P_2 - P_1)/RT$$

$$B(P_2 - P_1)/RT = (G_2 - G_1)/RT - \ln(P_2/P_1)$$

$$B(20 - 10)(\text{bar}) / [(83.14 \text{ bar cm}^3/\text{mol K})(300\text{K})] = (1466 \text{ J/mol}) / [(8.314\text{J/molK})(300\text{K})] - \ln(20/10)$$

$$B = -263 \text{ cm}^3 / \text{mol}$$