Graphical Methods for Phase Equilibrium

Class 20

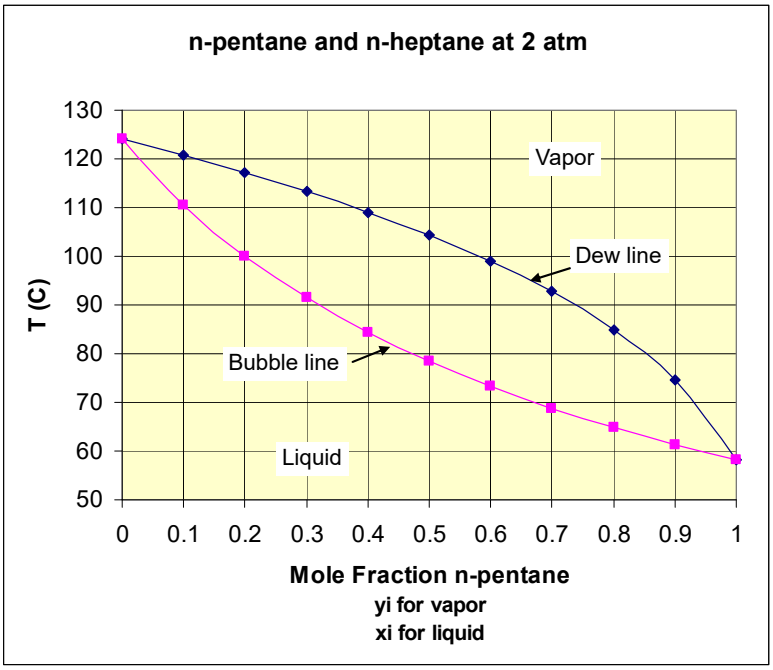
- Questions about Raoult's Law
  - Dew point
  - Bubble point
  - Flash
- Graphical methods
  - Vapor-liquid
  - Lever Rule
  - Solid-liquid
  - Liquid-liquid

1

Review

- If you know the composition in the gas phase
  - Dew Point
  - Does not matter how much liquid there is!
- If you know the composition in the liquid phase
  - Bubble point
  - Does not matter how much vapor there is!

2



Generated from Raoult's law using the DIPPR vapor pressure correlations

3

How was this chart generated?

(2 different ways)

1. Pick a mole fraction of pentane
   - Calculate dew point T
   - Calculate bubble point T
2. Pick a mole fraction of pentane
   - At each temperature, do a flash calculation

- T_{dp}:

$$1 = \sum x_i = \sum \frac{y_i P_{tot}}{P_i^*}$$

- T_{bp}:

$$P_{tot} = \sum x_i P_i^*$$

- Flash:

$$x_p = \frac{P_{tot} - P_h^*}{P_p^* - P_h^*}$$

$$y_p = \frac{x_p P_p^*}{P_{tot}}$$

4

How was this chart generated?

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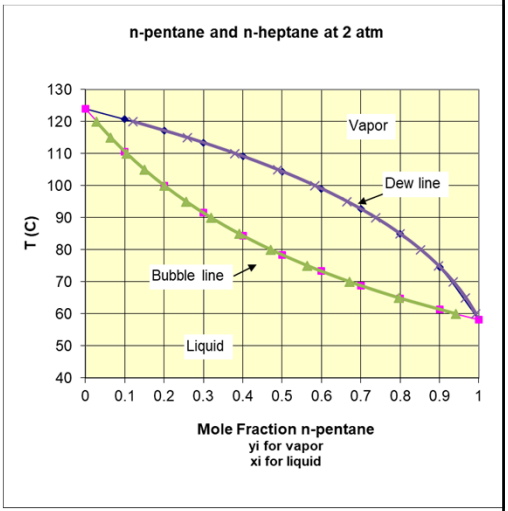
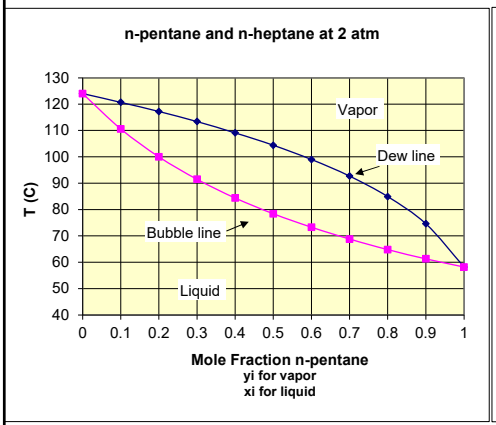
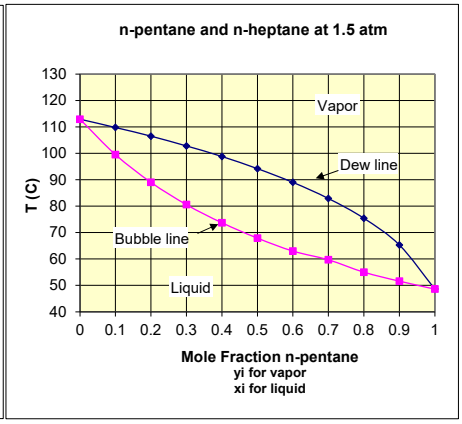


5



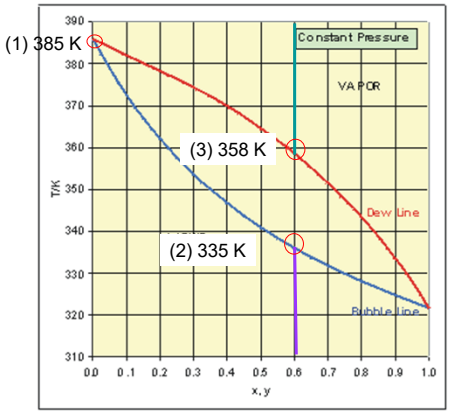


6

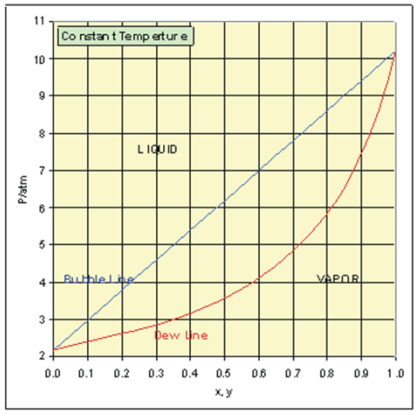
VLE Phase Diagrams

(n-pentane/n-heptane)

1) What is the boiling point of n-heptane?
2) At what temperature would a liquid mixture of 40% n-heptane and 60% n-pentane begin to boil?
3) At what temperature would a vapor mixture of 40% n-heptane and 60% n-pentane begin to condense?



Mole fraction pentane
(at 1.5 atm)



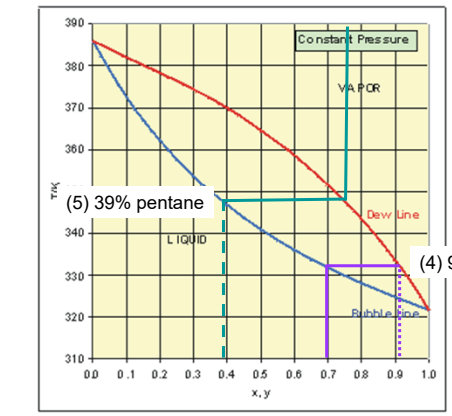
Mole fraction pentane
(at 400 K)

7

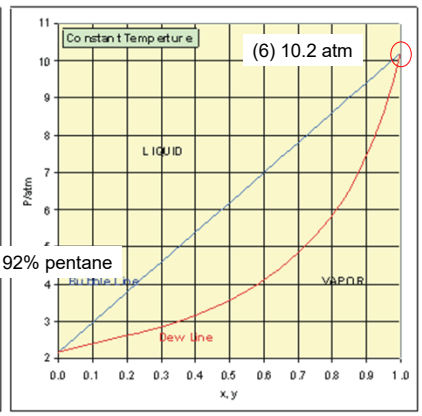
VLE Phase Diagrams

(n-pentane/n-heptane)

4) What is the composition of the vapor in equilibrium with a liquid that is 30% n-heptane and 70% n-pentane?
5) What is the composition of the liquid in equilibrium with a vapor that is 75% n-pentane and 25% n-heptane?
6) Using the P-xy diagram, what is the vapor pressure of n-pentane at the temperature for which the diagram was prepared?



Mole fraction pentane
(at 1.5 atm)

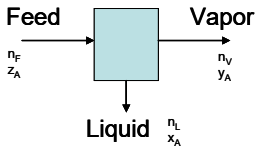


Mole fraction pentane
(at 400 K)

8

Lever Rule

2 distinct phases and 2 components

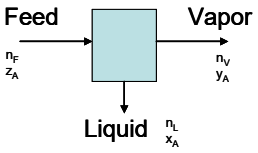


- Total mole balance: $n_F = n_L + n_V$
  (or $n_V = n_F - n_L$)
- Species mole balance $z_A n_F = x_A n_L + y_A n_V$
- Now substitute for n_V $z_A n_F = x_A n_L + y_A (n_F - n_L)$
- Group n_F terms on left and n_L terms on right
  $(z_A - y_A) n_F = (x_A - y_A) n_L$ $\frac{n_L}{n_F} = \frac{z_A - y_A}{x_A - y_A} = \frac{y_A - z_A}{y_A - x_A}$

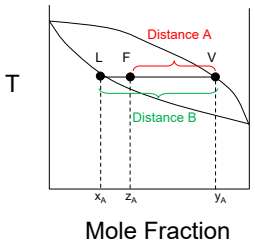
9

Lever Rule

Graphical Interpretation (very useful)



$$\frac{n_L}{n_F} = \frac{z_A - y_A}{x_A - y_A} = \frac{y_A - z_A}{y_A - x_A}$$



- Distance A corresponds to $y_A - z_A$.
- Distance B corresponds to $y_V - x_A$.
- Therefore, n_L/n_F = Distance A / Distance B!!
- In practice, you can use the actual mole fractions or use the measured distance using a ruler

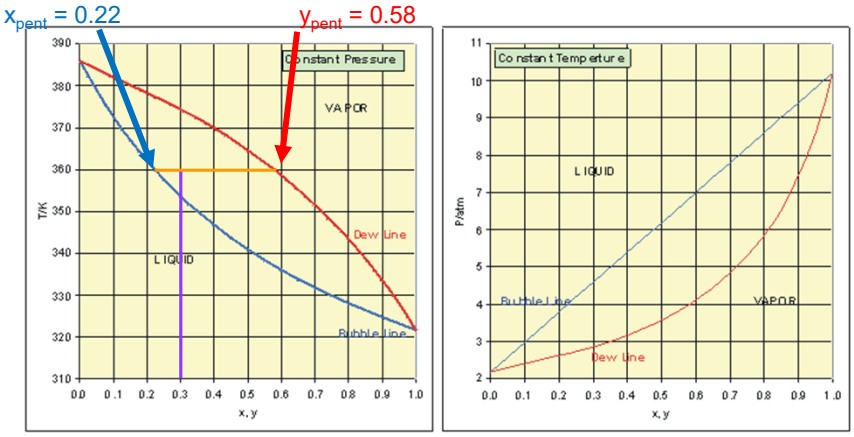
Intuition: As you get closer to the liquid line, you have more liquid!

10

VLE Phase Diagrams

(n-pentane/n-heptane)
part (7)

7) A feed stream of 30% n-pentane and 70% heptane is brought to a pressure of 1.5 atm and a temperature of 360 K. What is the composition and amount of the liquid and the vapor streams in equilibrium at this condition?



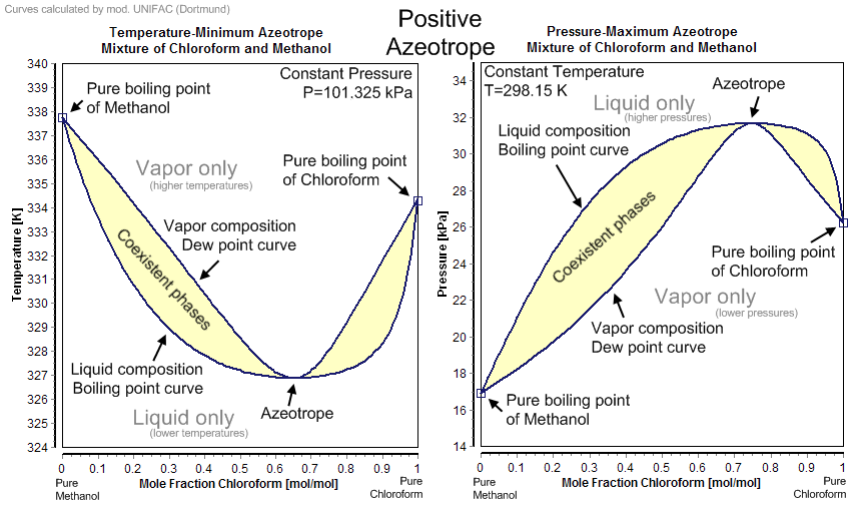
Mole fraction pentane
(at 1.5 atm)

Mole fraction pentane
(at 400 K)

Use lever rule. L/F = (0.58 – 0.3)/(0.58 – 0.22) or 2.8 boxes/(2.8 + 0.8) = 0.78

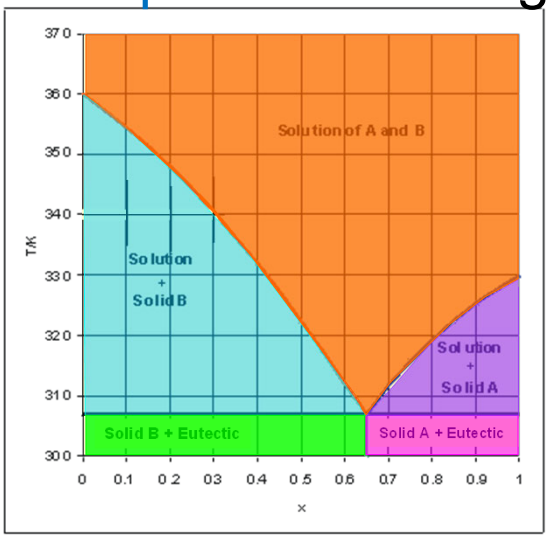
11

Non-ideal VLE behavior



12

Solid-Liquid Phase Diagrams



Mole fraction of A

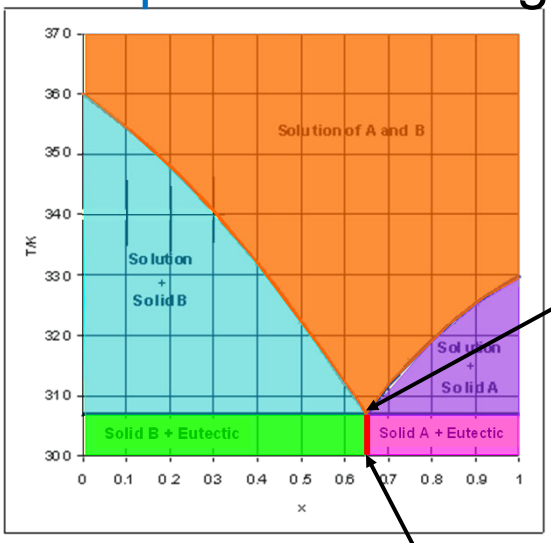
13

What is a Eutectic???

- Solid crystals having a composition that is a mixture of pure components
- Not in equilibrium with any liquid solution, but may be in equilibrium with a pure solid
  - i.e., a fraction of the solid is pure component, and the rest is the crystals with mixed composition

14

Solid-Liquid Phase Diagrams



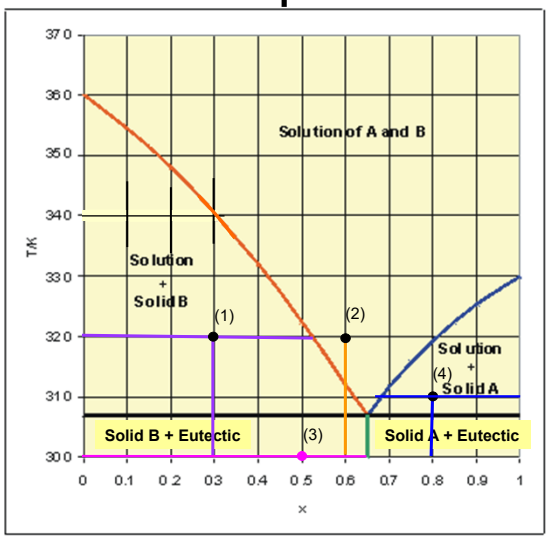
Eutectic point (no liquid below this temperature)

Mole fraction of A

Eutectic composition

15

Solid-Liquid Phase Diagrams



Mole fraction of A

1) What phases are present for a mixture of 30% A at 320 K?
2) What phases are present for a mixture of 60% A at 320 K?
3) What phases are present for mixture of 50% A at 300 K?
4) For a mixture of 80% A, what phases are present at equilibrium at 310 K? How much of each phase is present?

1) Pure Solid B and solution with 52% A
2) Solution with 60% A
3) Solid B and solid eutectic of 65% A
4) Solid A and solution with 68% A
   2/3.2 = 62.5% of material is solution, 37.5% solid A

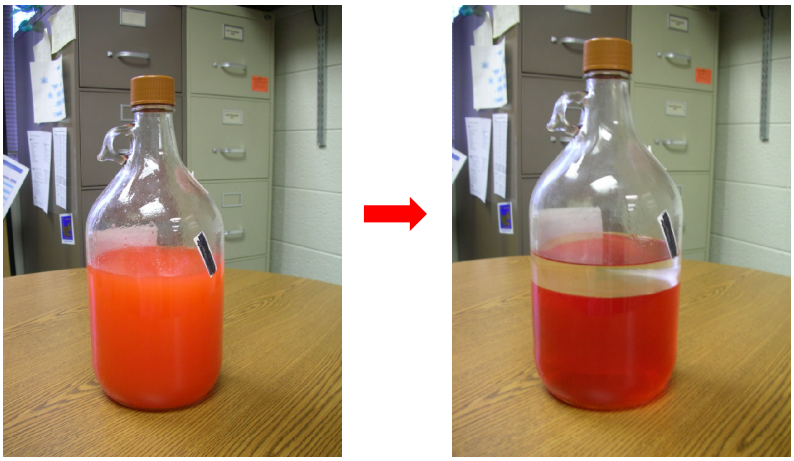
16

Liquid-Liquid Equilibrium

17

Butanol-Water Demo

(Liquid-Liquid Equilibrium)

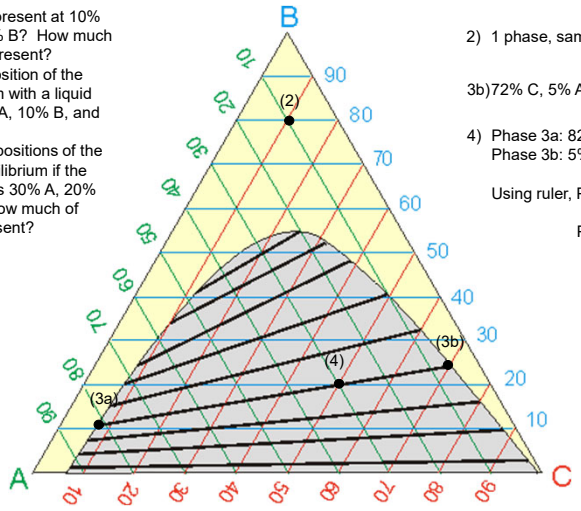


18

Liquid-Liquid Ternary Phase Diagram

(these may be found in either mole% or wt%)

1) What does the dark region represent?
2) What phase(s) is present at 10% A, 10% C and 80% B? How much of each phase is present?
3) What is the composition of the liquid in equilibrium with a liquid consisting of 82% A, 10% B, and 8% C?
4) What are the compositions of the two phases in equilibrium if the total composition is 30% A, 20% B, and 50% C? How much of each phase is present?



1) 2-phase region

2) 1 phase, same composition

3b)72% C, 5% A, 23% B

4) Phase 3a: 82% A, 10% B, 8% C
Phase 3b: 5% A, 23% B, 72% C

Using ruler, Phase 3a = 2.4 cm/7.7 cm
= 31%
Phase 3b = 69%

19