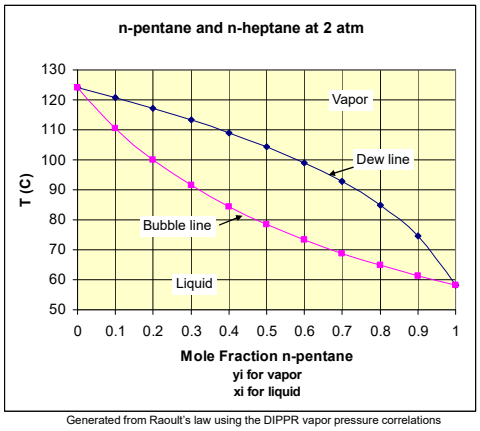
Graphical Methods for Phase Equilibrium
Class 21

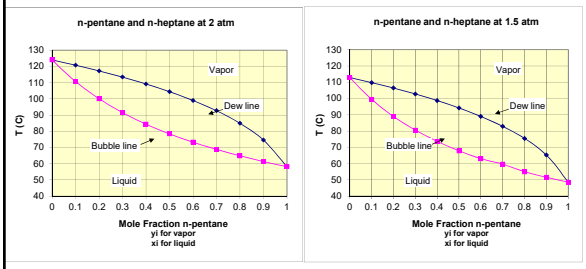
- Questions about Raoult's Law
  - Dew point
  - Bubble point
  - Flash
- Graphical methods
  - Vapor-liquid
  - Lever Rule
  - Solid-liquid
  - Liquid-liquid

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!

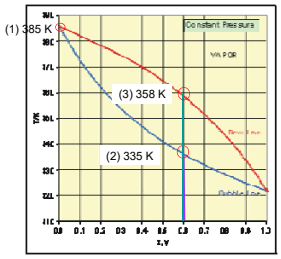


Generated from Raoult's law using the DIPPR vapor pressure correlations

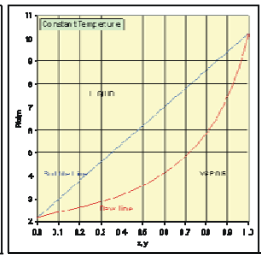


VLE Phase Diagrams
(n-pentane/n-heptane)

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?



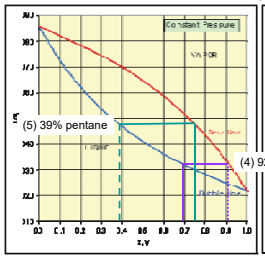
Mole fraction pentane
(at 1.5 atm)



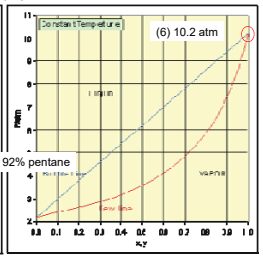
Mole fraction pentane
(at 400 K)

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?



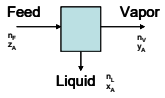
Mole fraction pentane
(at 1.5 atm)



Mole fraction pentane
(at 400 K)

Lever Rule

2 distinct phases and 2 components

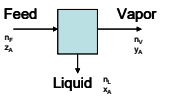


- Total mole balance: $n_F = n_L + n_V$ (or $n_V = n_F - n_L$)
- Species mole balance $z_A n_F = x_A n_L + y_A n_V$
- Now substitute for n_V $z_A n_F = x_A n_L + y_A (n_F - n_L)$
- Group n_F terms on left and n_L terms on right

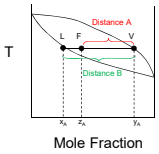
$(z_A - y_A) n_F = (x_A - y_A) n_L$ $\quad \frac{n_L}{n_F} = \frac{z_A - y_A}{x_A - y_A} = \frac{y_A - z_A}{y_A - x_A}$

Lever Rule

Graphical Interpretation (very useful)



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



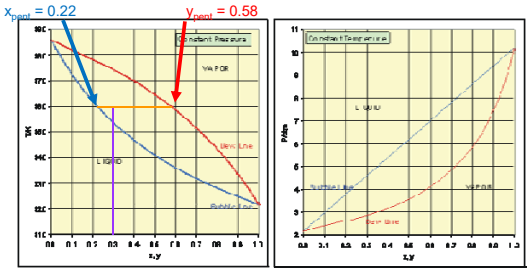
- Distance A corresponds to $y_A - z_A$.
- Distance B corresponds to $y_V - x_A$.
- Therefore, n_L/n_F = Distance A / Distance B!!
- In practice, you can use the actual mole fractions or use the measured distance using a ruler

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

VLE Phase Diagrams

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

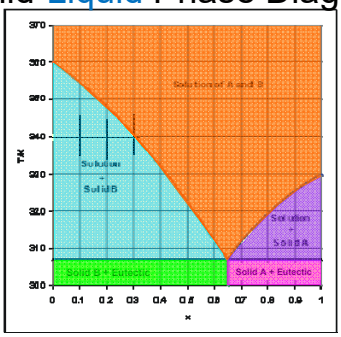
7) A feed stream of 30% n-pentane and 70% heptane is brought to a pressure of 1.5 atm and a temperature of 360 K. What is the composition and amount of the liquid and the vapor streams in equilibrium at this condition?



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

Solid-Liquid Phase Diagrams

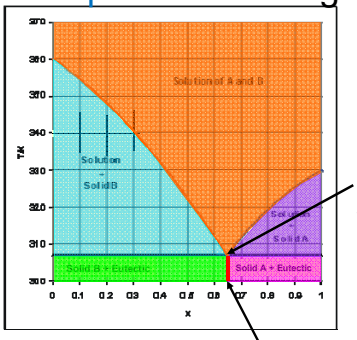


Mole fraction of A

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

Solid-Liquid Phase Diagrams

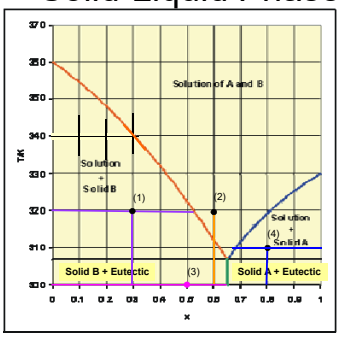


Eutectic point (no liquid below this temperature)

Mole fraction of A

Eutectic composition

Solid-Liquid Phase Diagrams



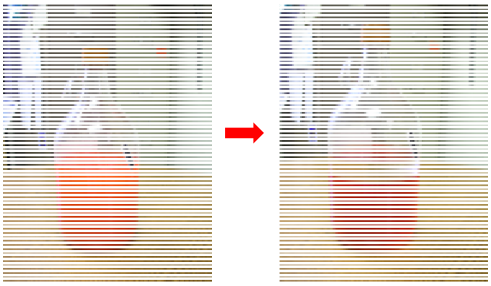
Mole fraction of A

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

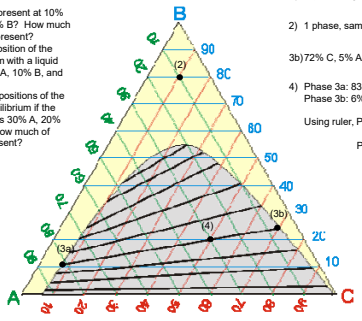
Liquid-Liquid Equilibrium

Butanol-Water Demo
(Liquid-Liquid Equilibrium)



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: 83% A, 11% B, 6% C
Phase 3b: 6% A, 24% B, 70% C
Using ruler, Phase 3a = 2.4 cm/7.7 cm = 31%
Phase 3b = 69%