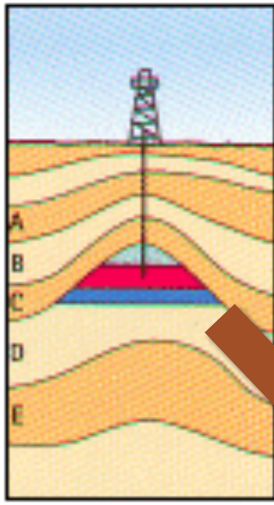
Lecture 4

Binary Phase Diagrams and Retrograde Behavior

Lectures 1-3



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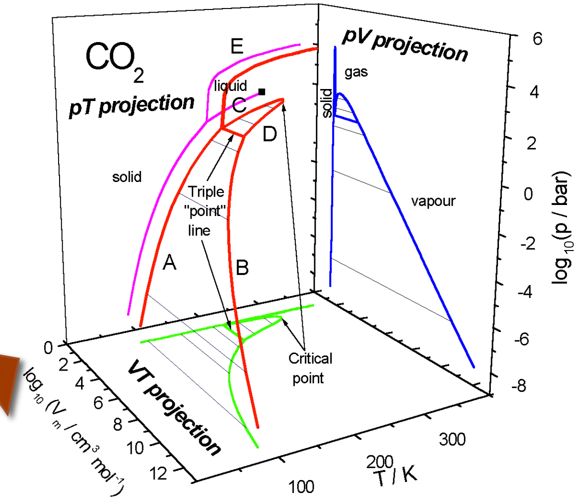
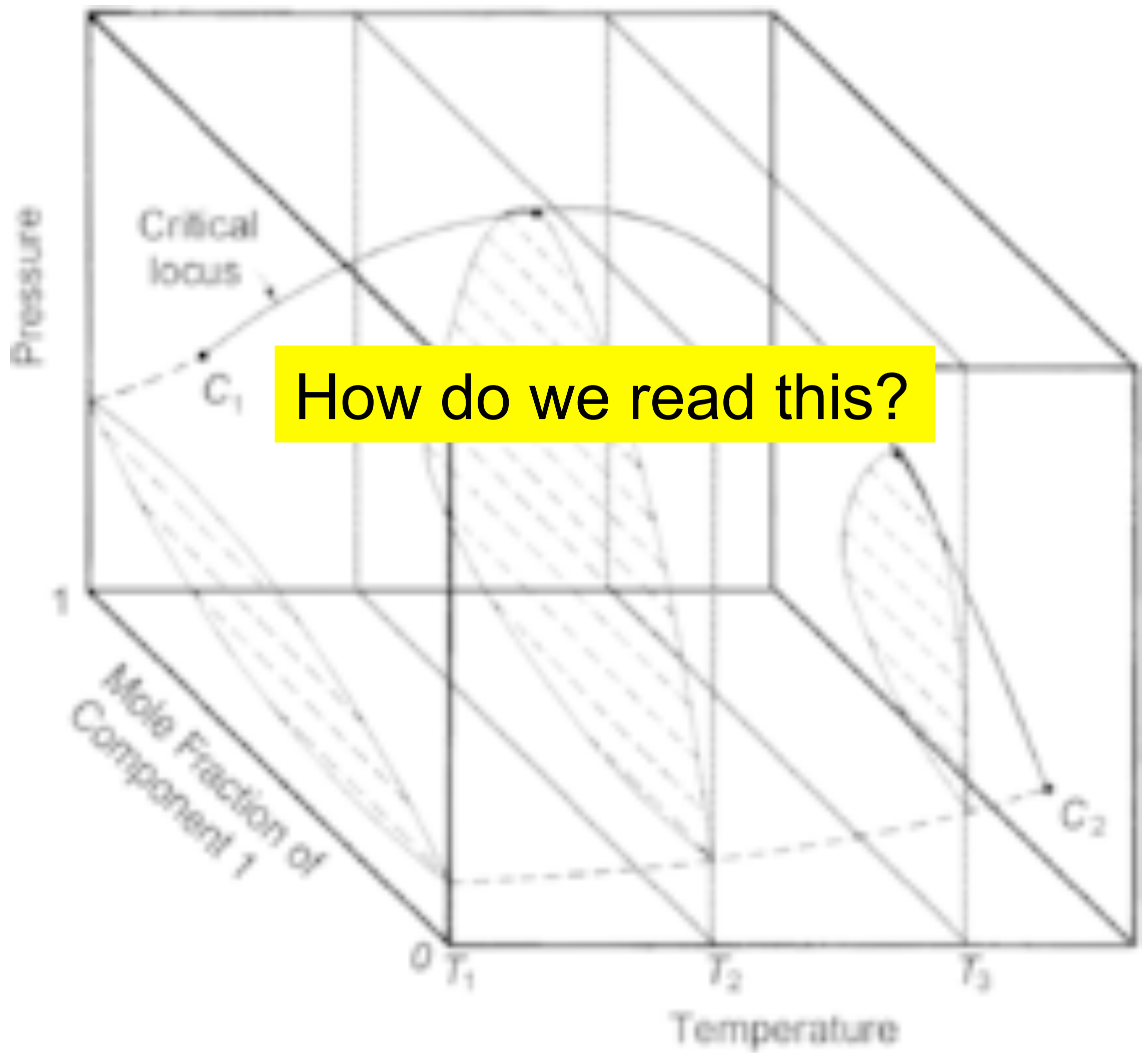


Crude Fraction	Boiling Point (ºF)	Composition	Uses
HC gas	< 100	C1 – C2 C3 – C4	Fuel gas Bottled fuel gas, solvent
Gasoline	100 – 350	C5 – C10	Motor fuel, solvent
Kerosene	350 – 450	C11 – C12	Jet fuel, cracking stock
Light gas oil	450 – 580	C13 – C17	Diesel fuel, furnace fuel
Heavy gas oil	480 – 750	C18 – C25	Lubricating oil, bunker foil
Lubricants, waxes	750 – 950, 100 (melt)	C26 – C38	Lubricating oil, paraffin wax, petroleum jelly
Residuum	950+, 200+ (melt)	C38+	Tars, roofing compounds, paving asphalts, coke

Binary Mixture Road Map

- Pressure-Temperature-composition diagram
  - PT Diagrams
    - Bubble points & dew points
    - Locus of Critical Points
  - Px and Tx diagrams
  - Retrograde Behavior

PTx Diagrams



How do we read this?

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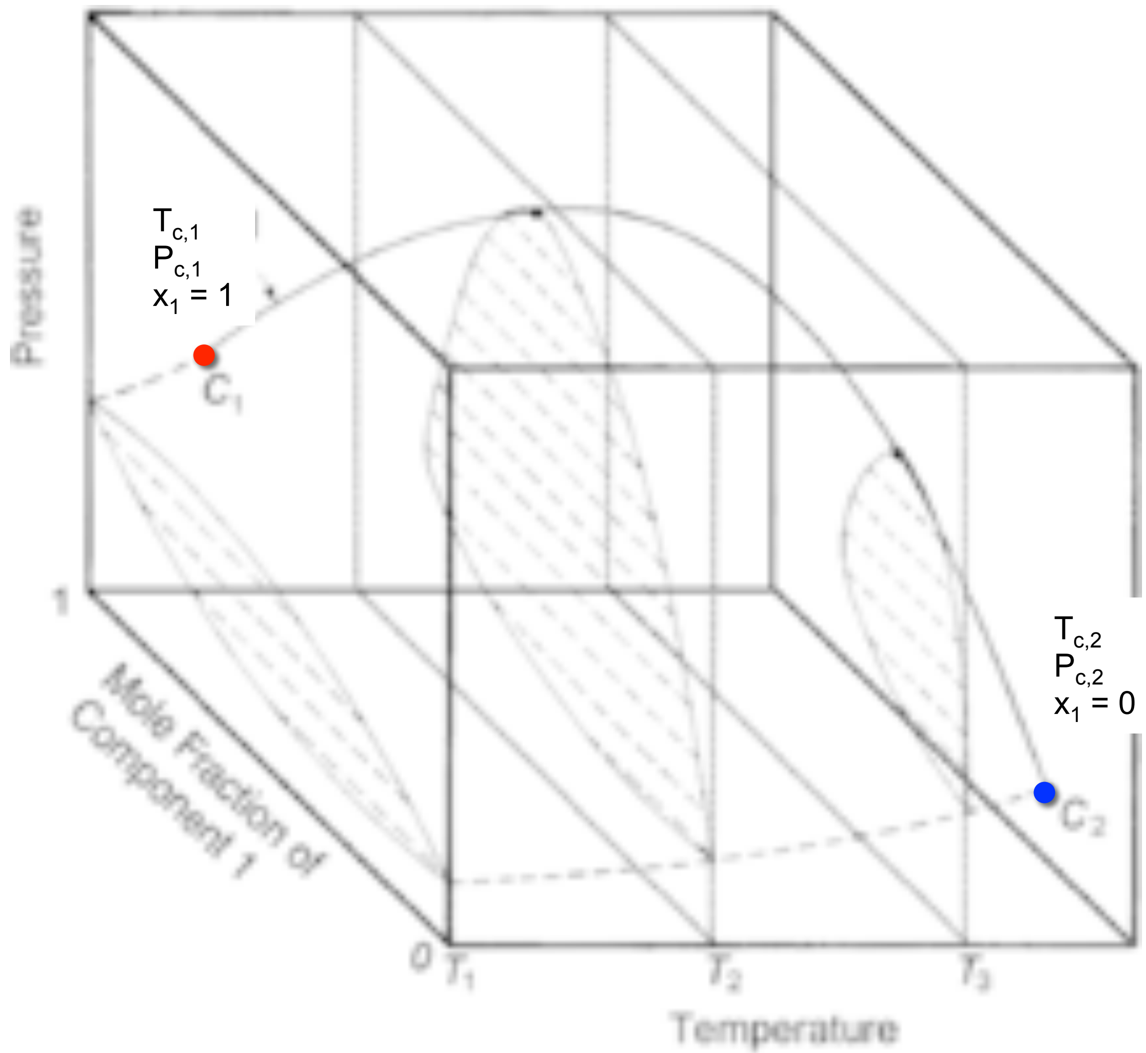
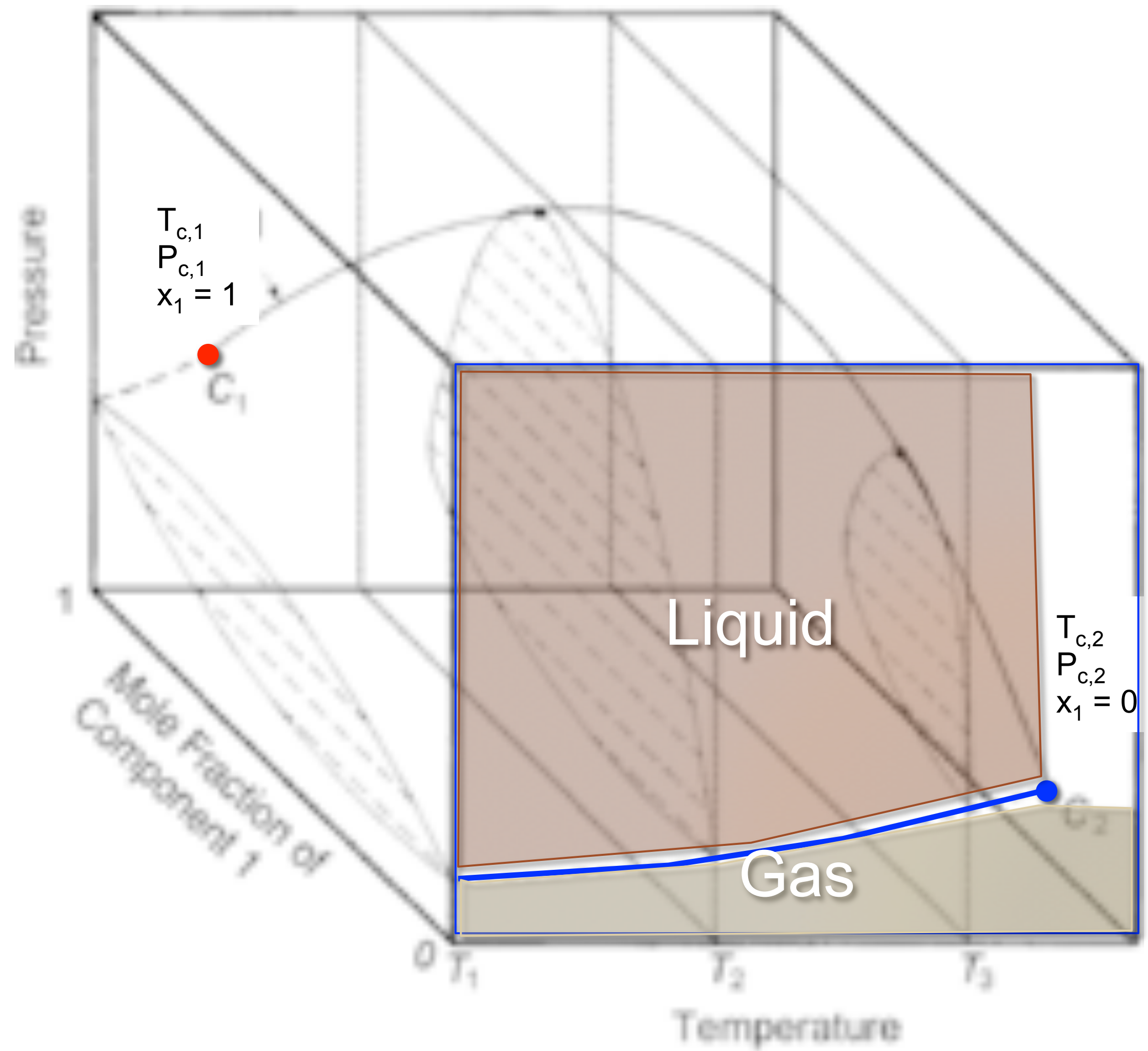
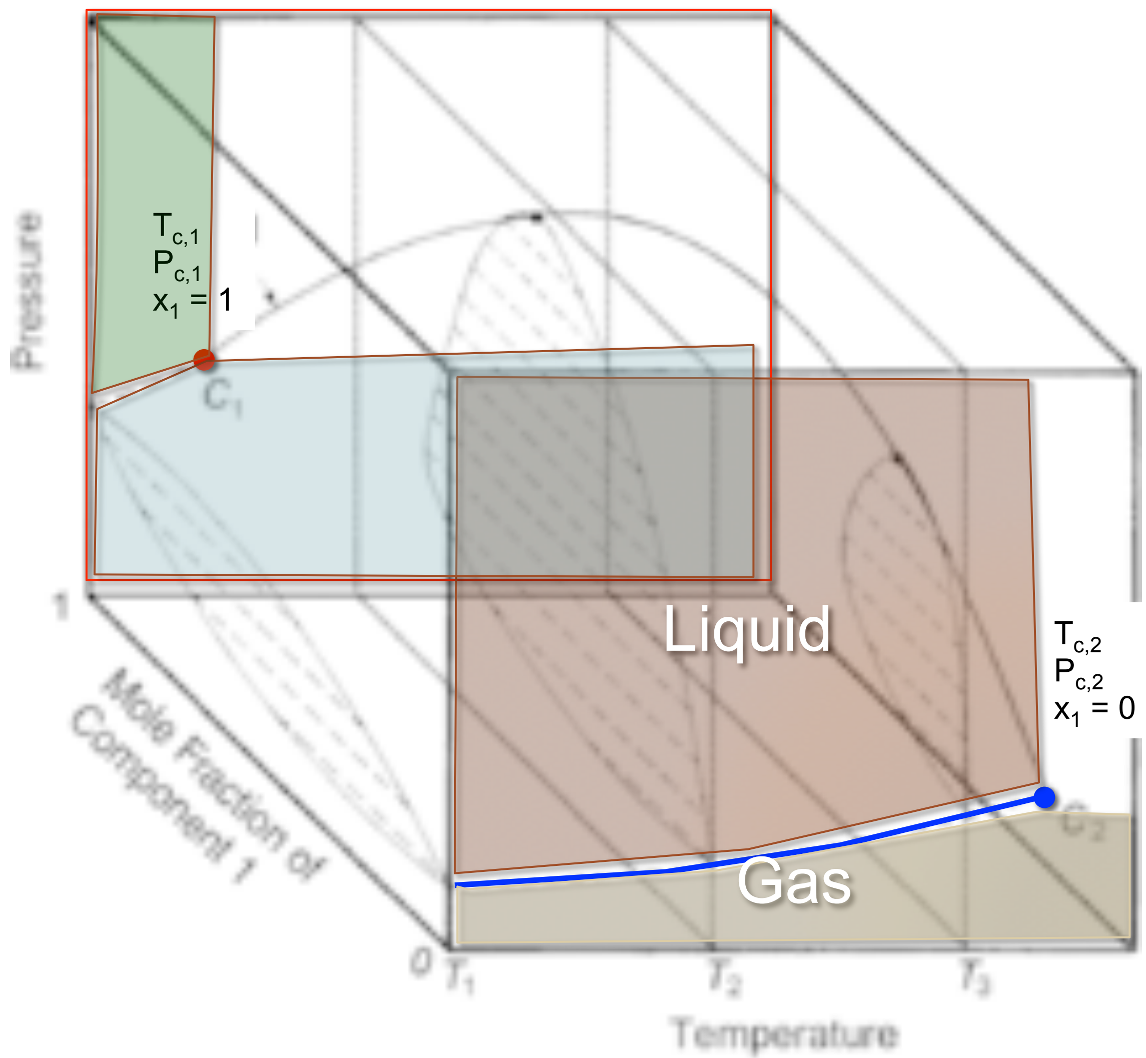
PTx Diagrams



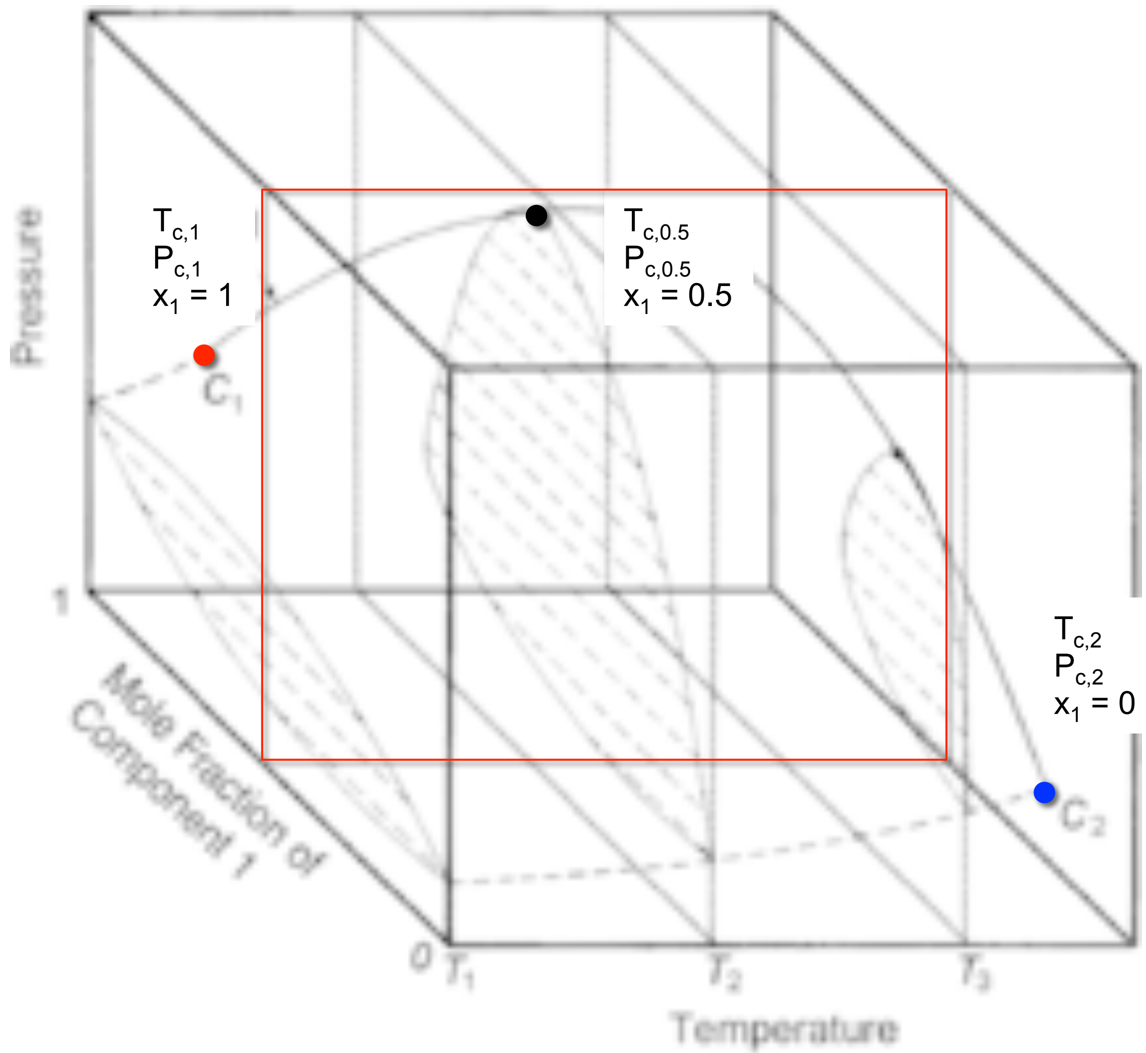
PTx Diagrams



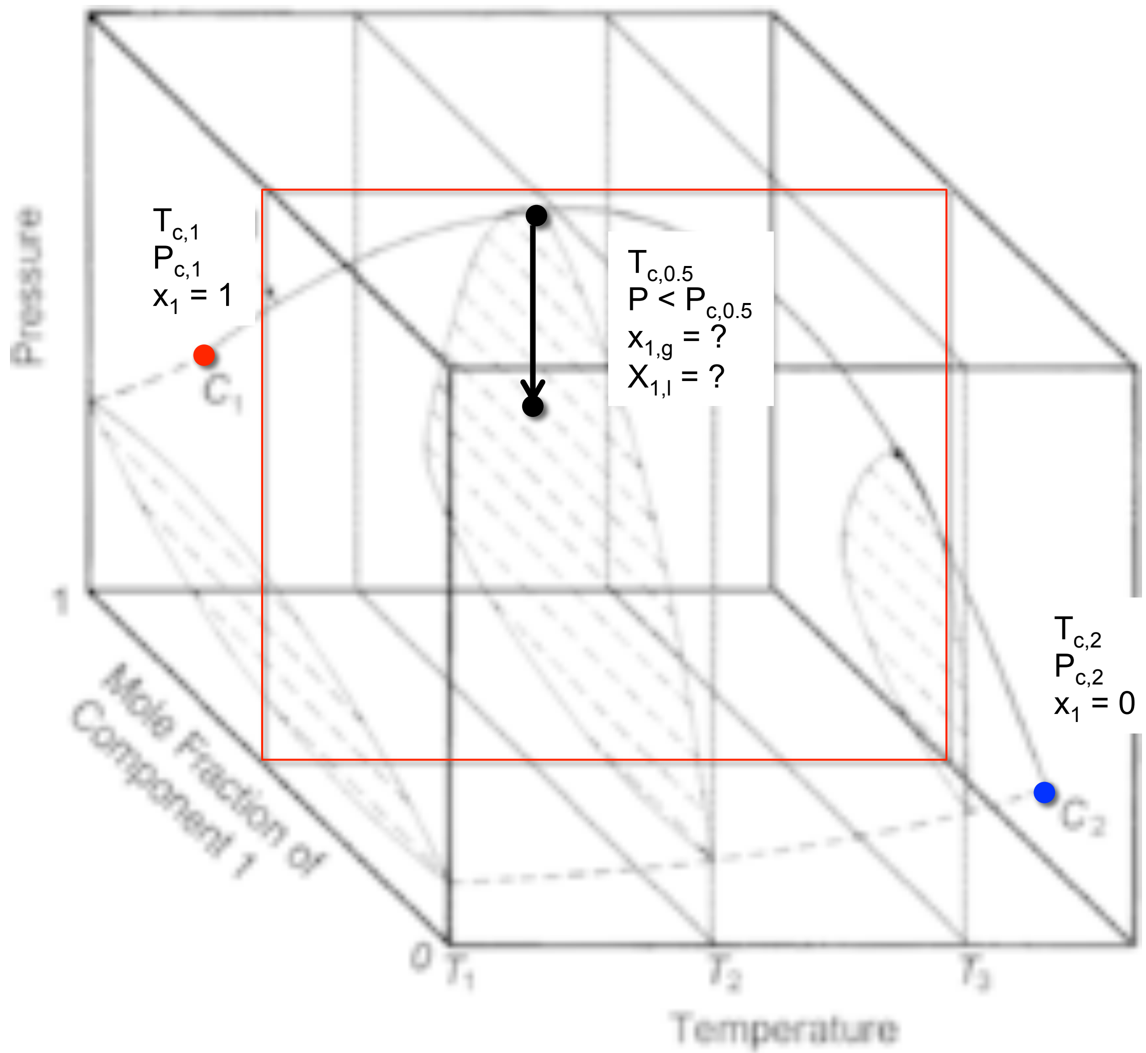
PTx Diagrams



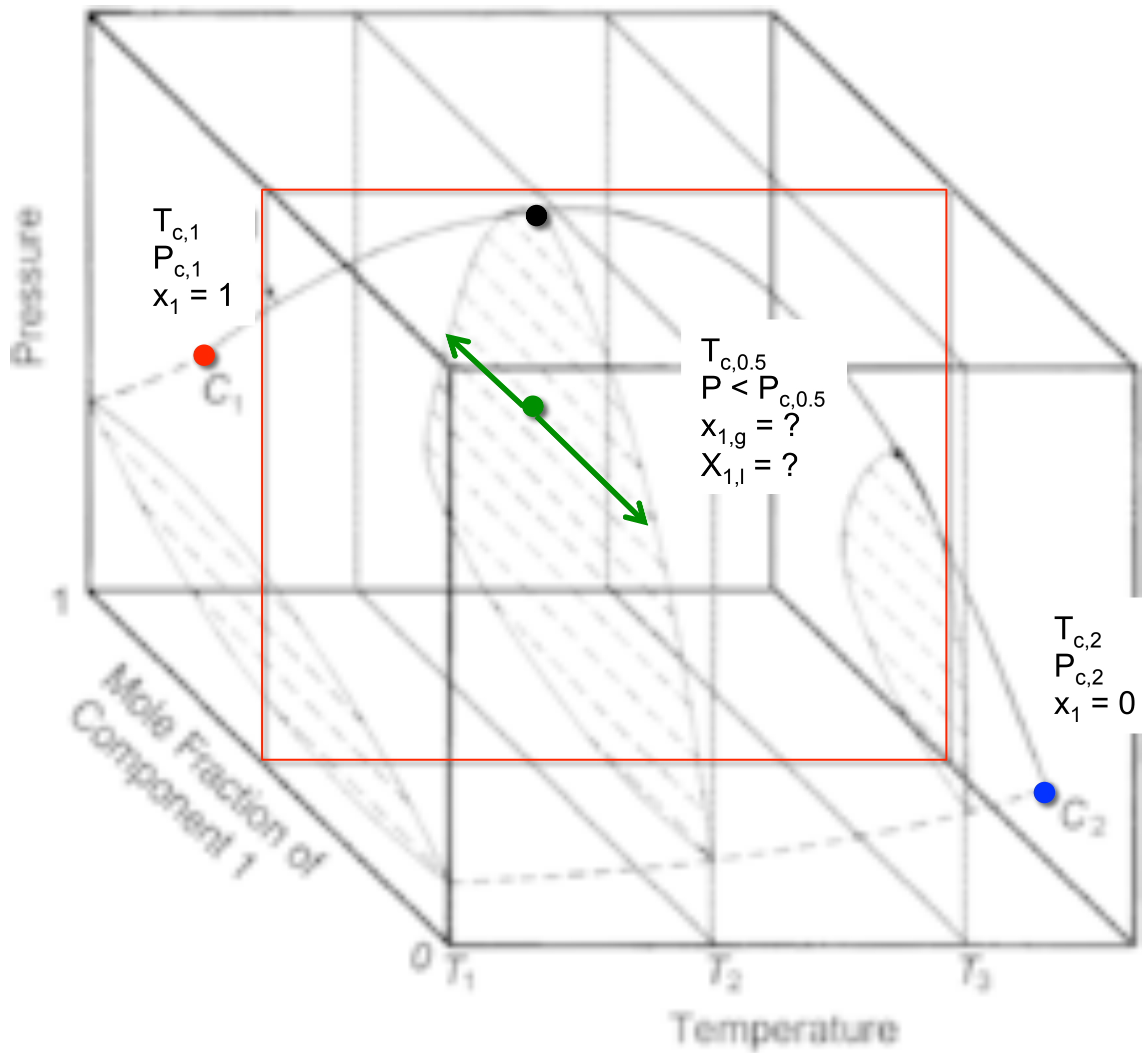
PTx Diagrams



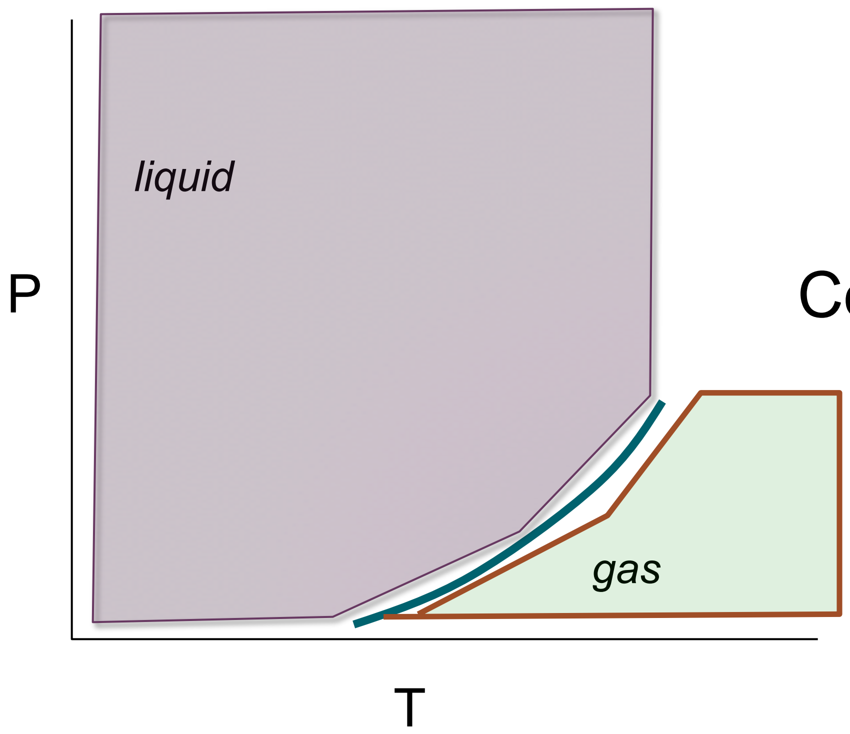
PTx Diagrams



PTx Diagrams

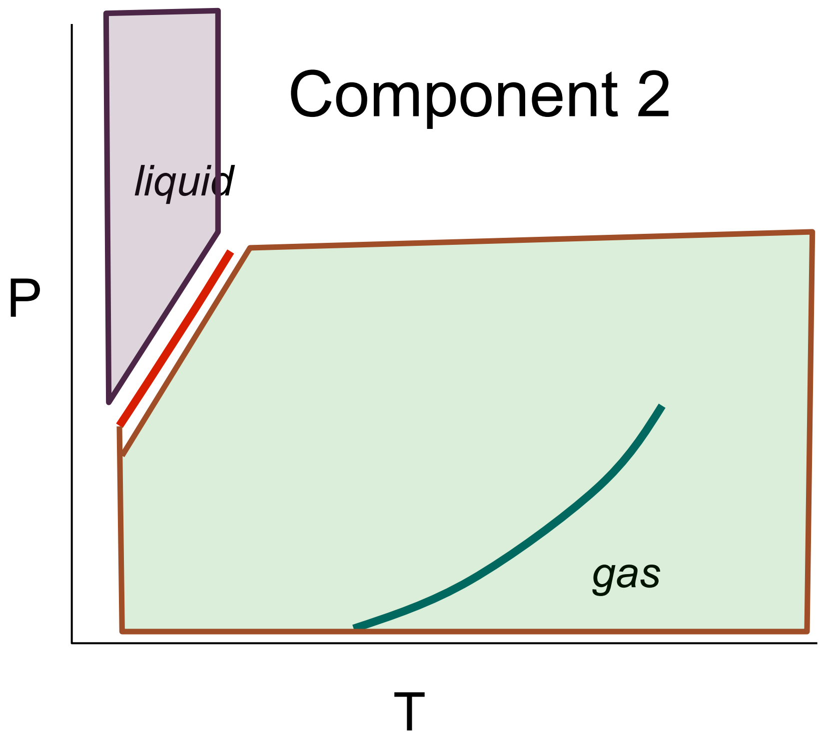


Binary PT Diagrams



Component 1

Binary PT Diagrams



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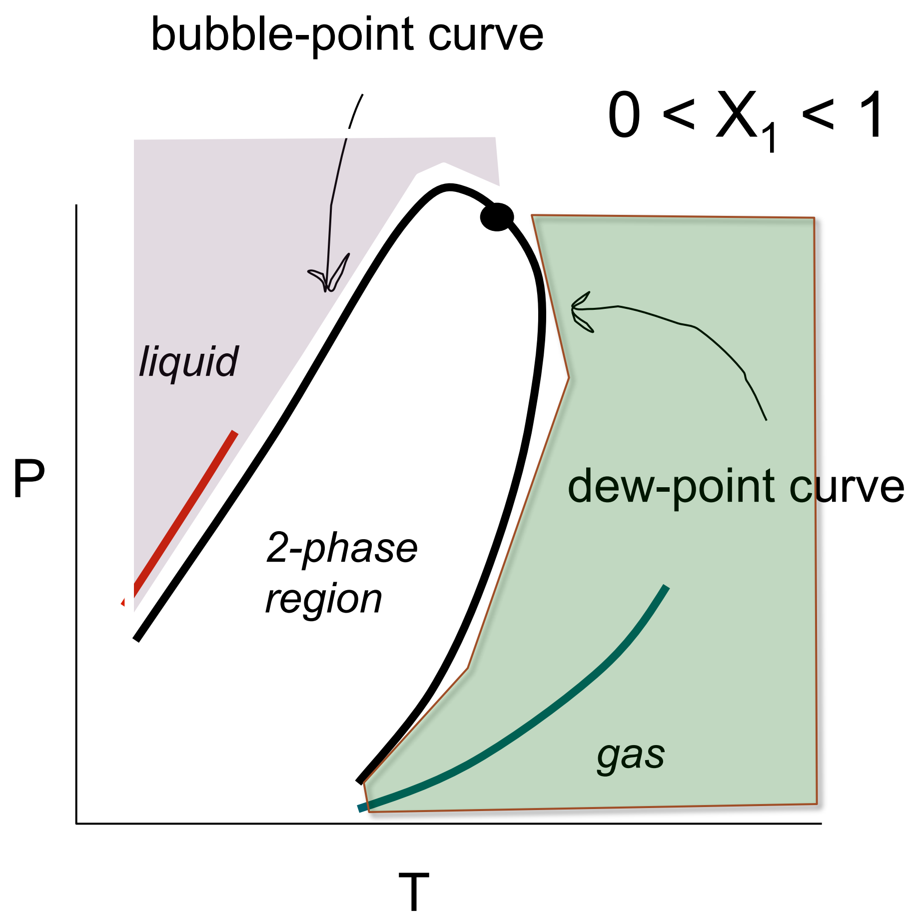
Binary PT Diagrams



T_c always between critical temperatures of the pure components

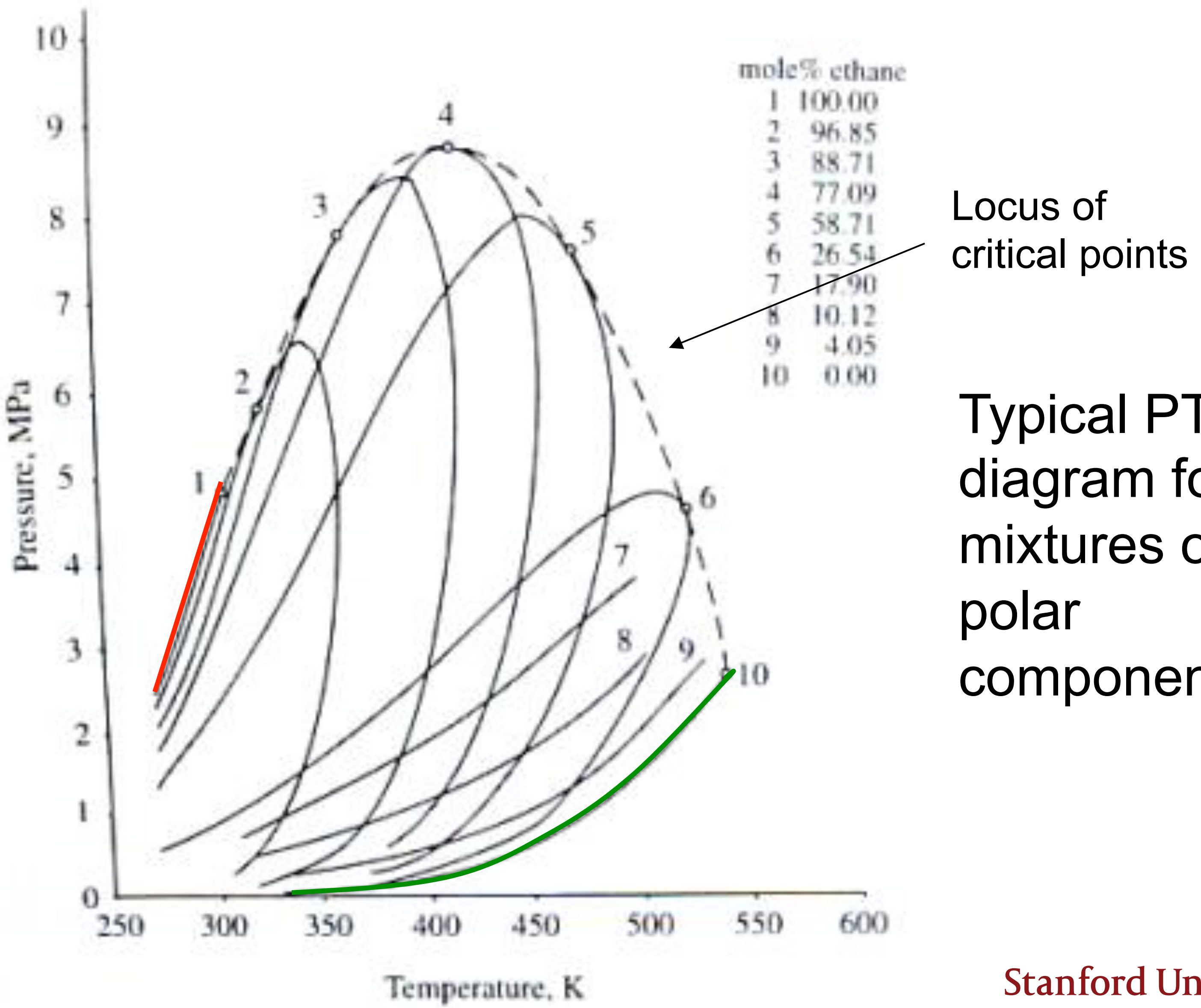
P_c well above critical pressures of the pure components

All mixtures are within the envelope between the two single component vapor-liquid equilibrium curve

How do the bubble and dew point curves differ from single component systems?

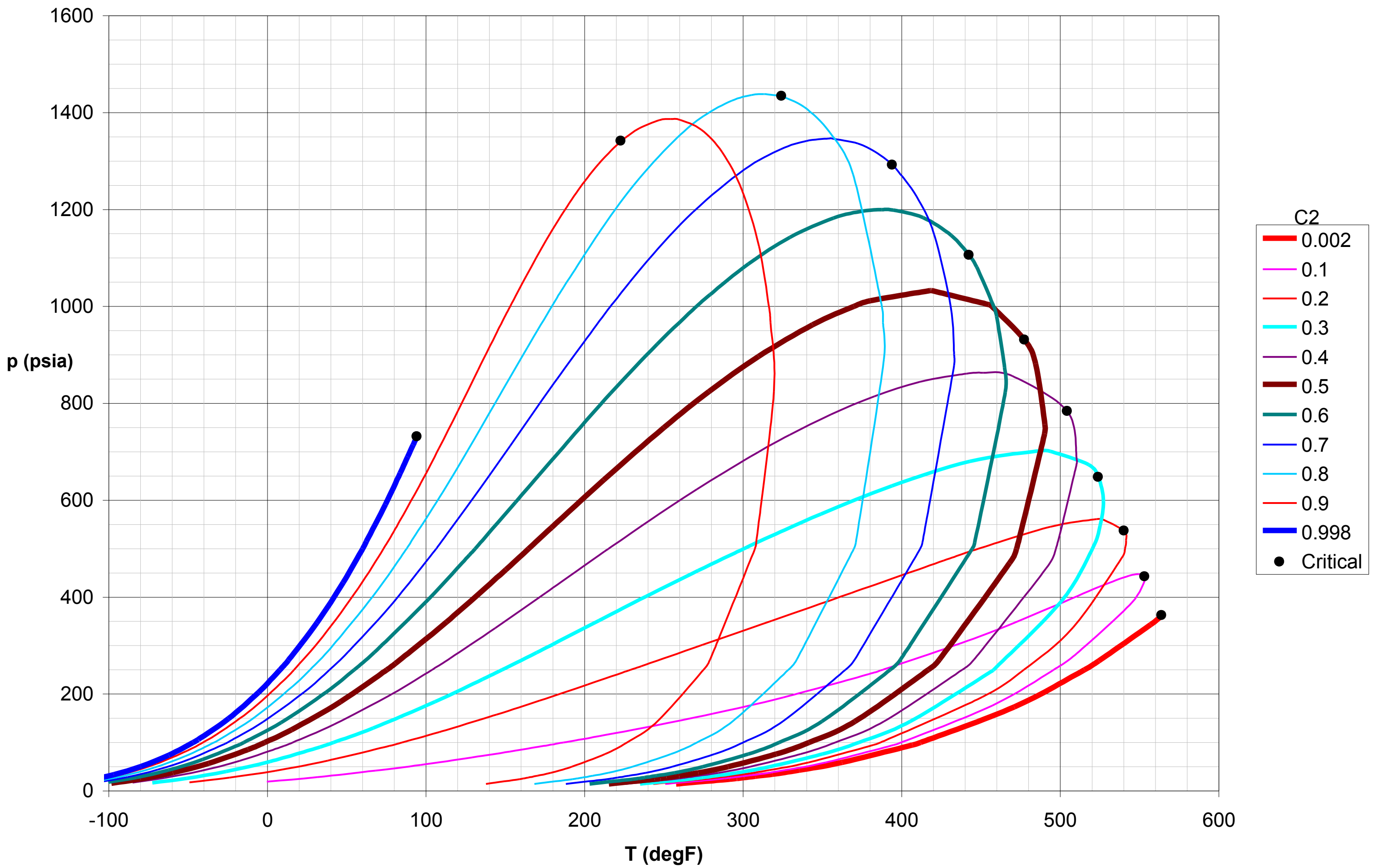
Binary PT Diagrams – ethane and n-heptane

P



Typical PT diagram for mixtures of non-polar components

Binary PT Diagrams – ethane and n-octane



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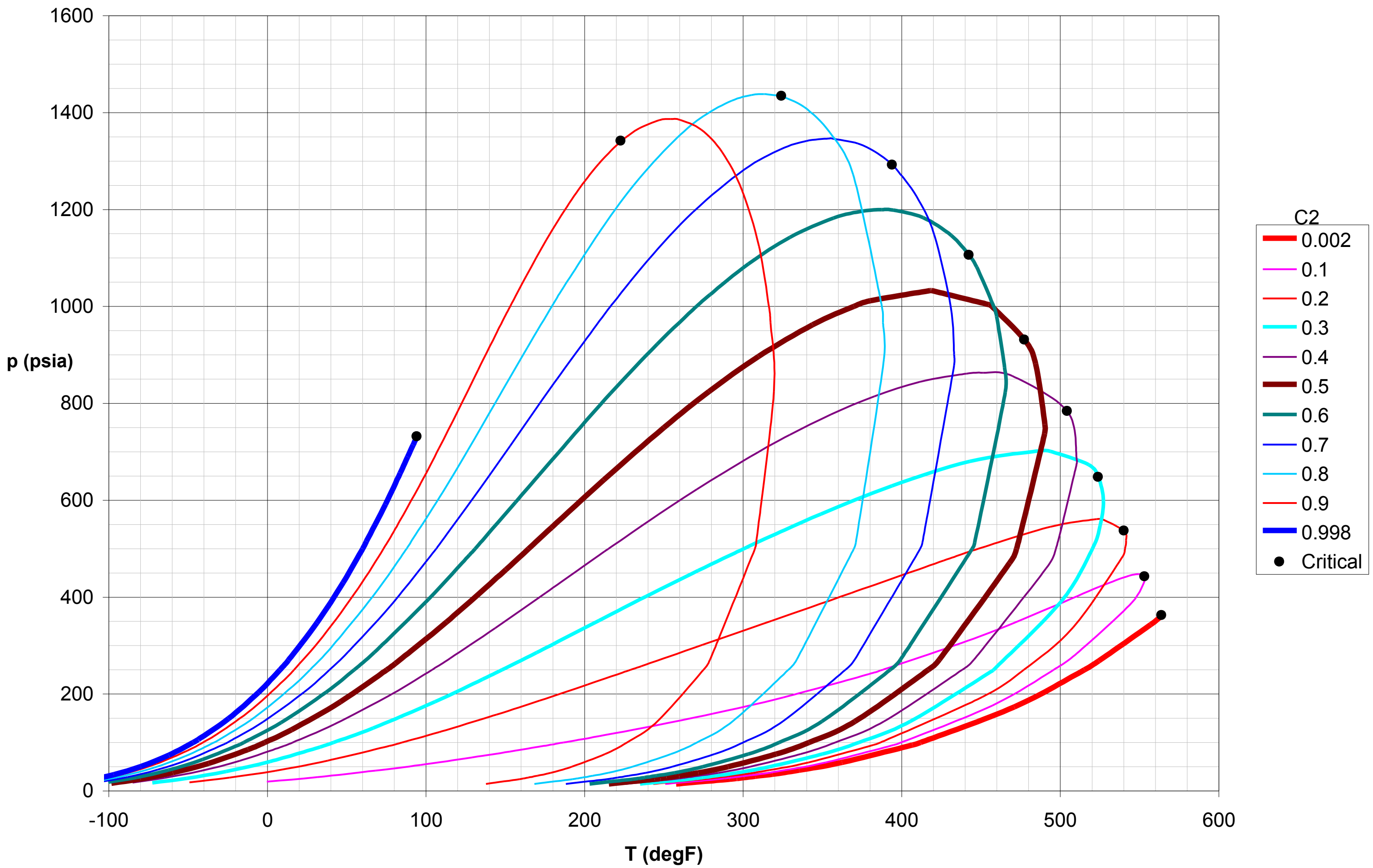
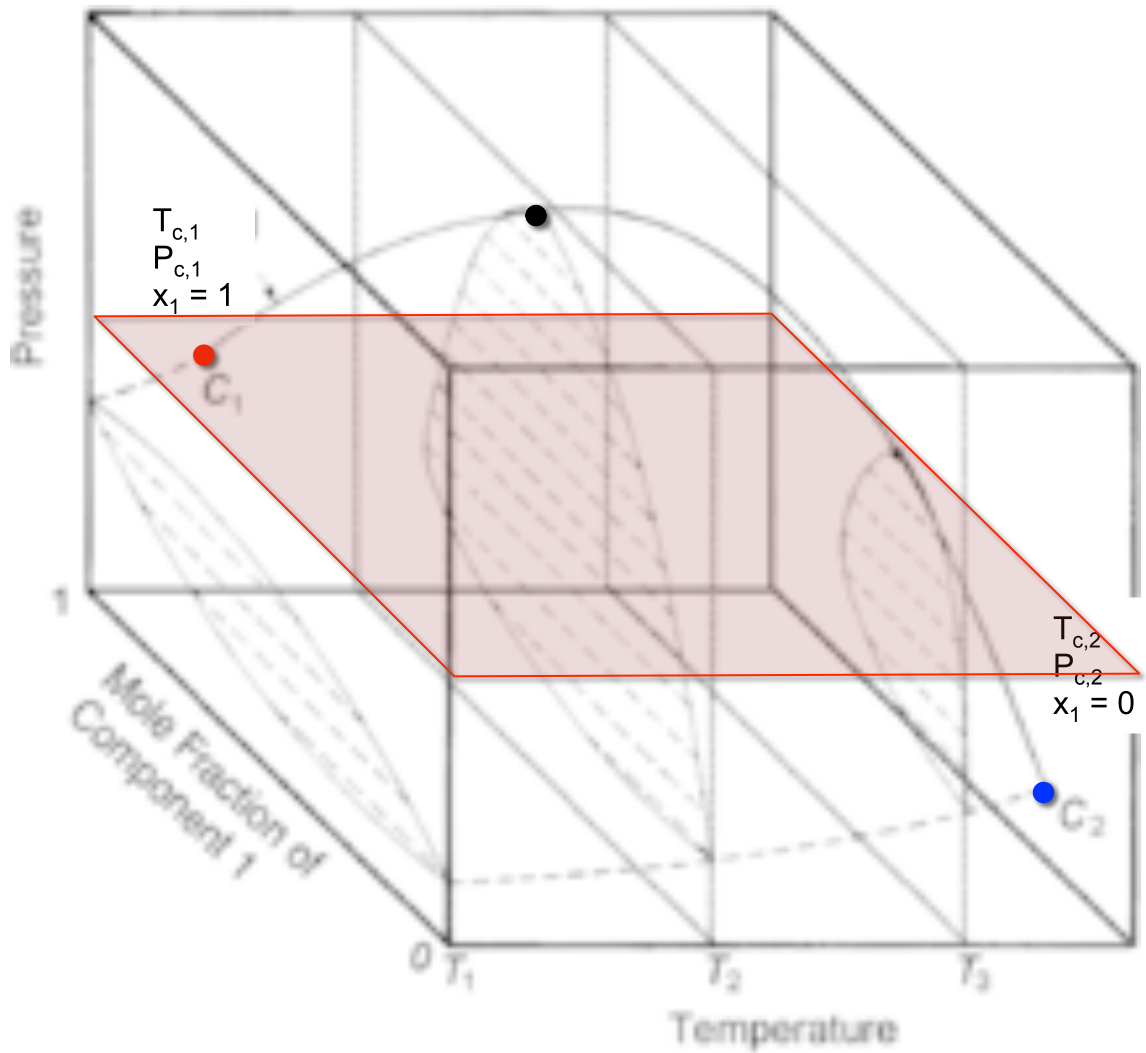
Binary PT Diagrams – ethane and n-heptane

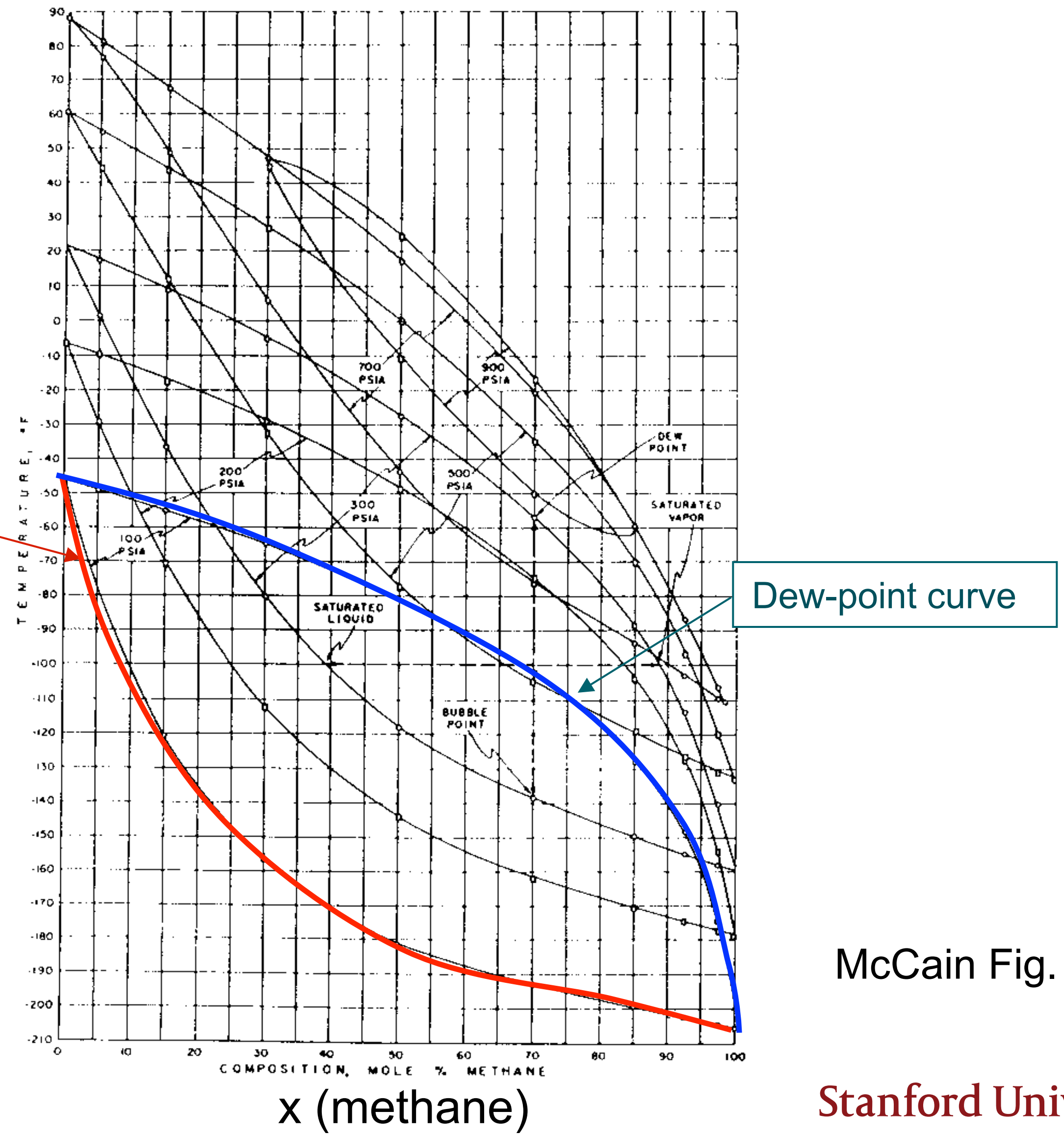


PTx Diagrams



Tx Diagram

x = 0.5
P = 100 psia
T = -120ºF



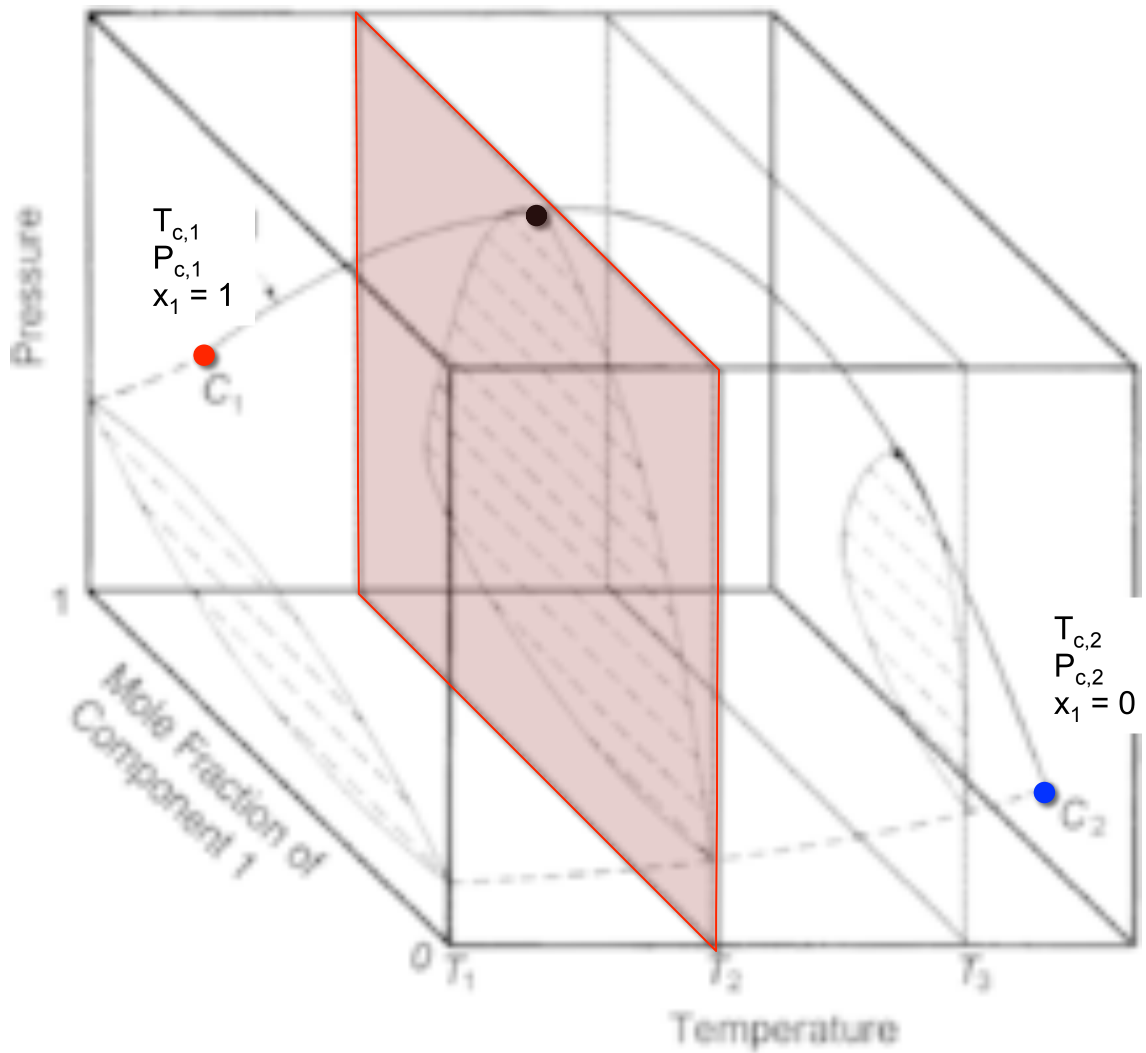
Note:

Bubble-point curve is the lower line

Dew-point curve is the upper line

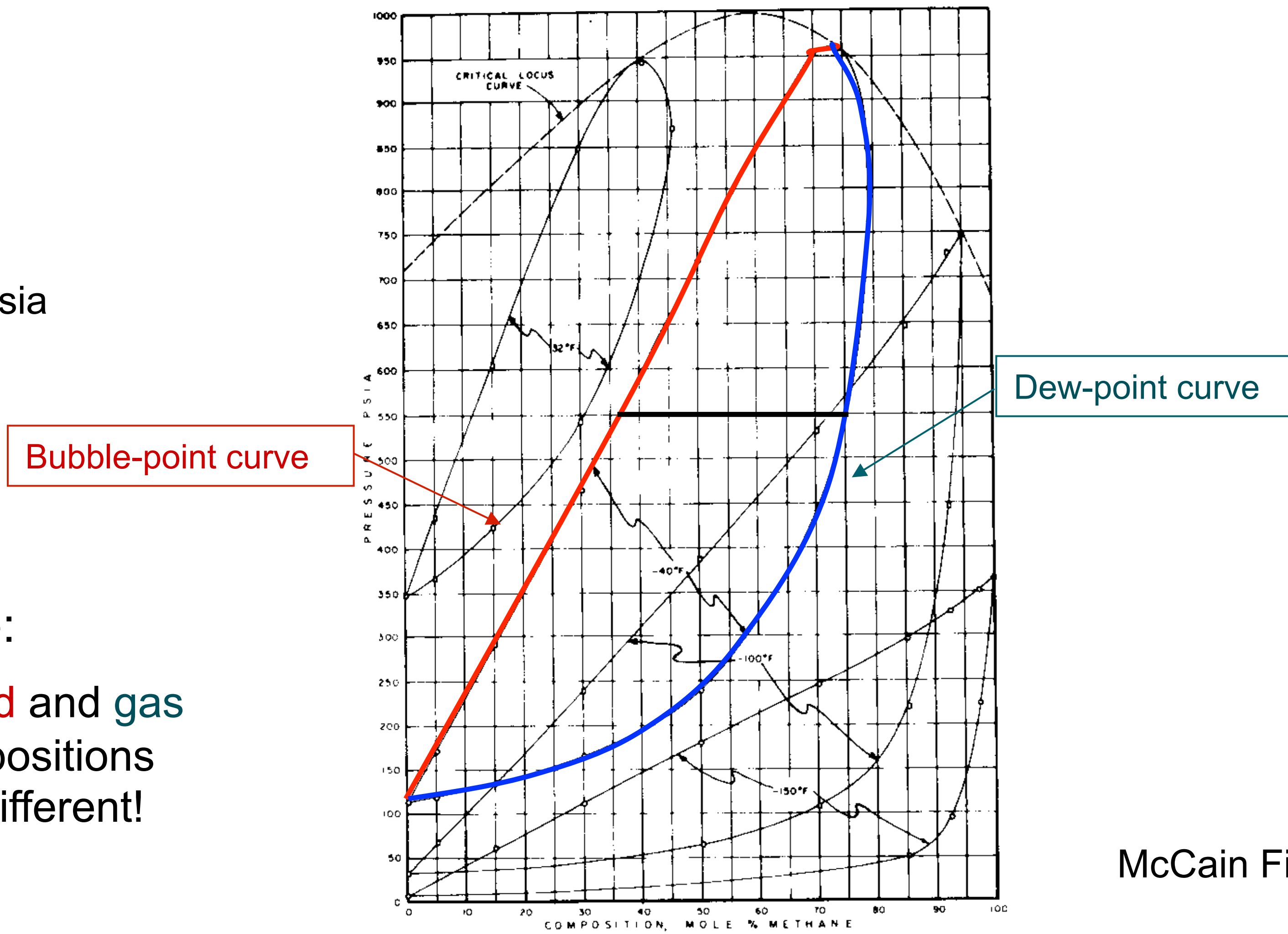
McCain Fig. 2-24

PTx Diagrams



Px Diagram

x = 0.5
P = 500 psia
T = -40ºF



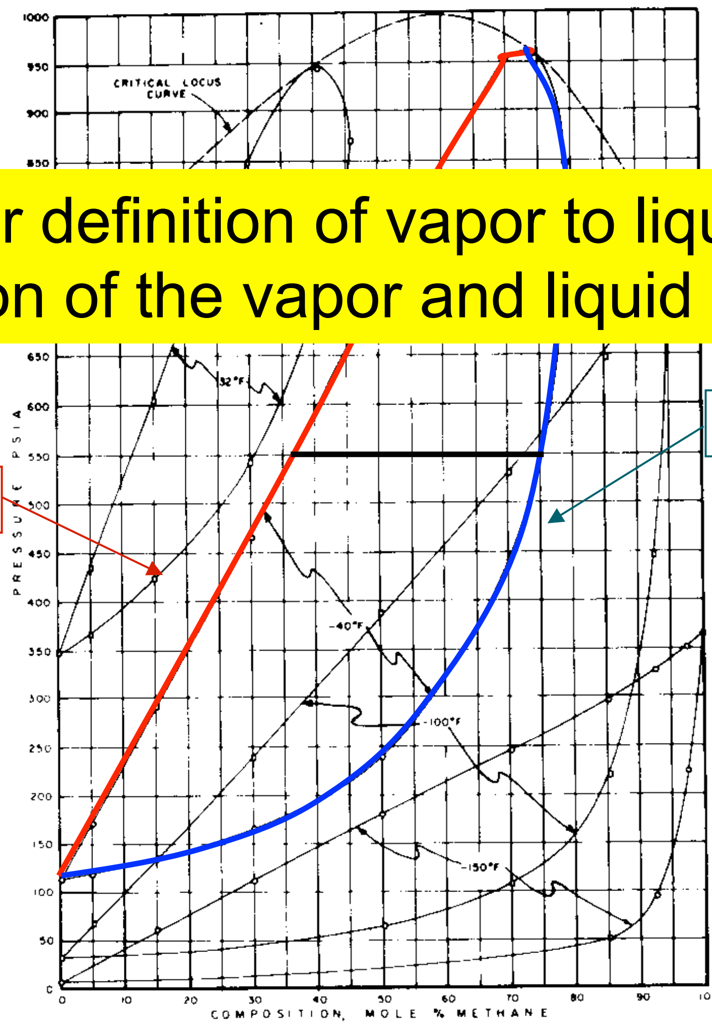
x (methane)

McCain Fig. 2-22

Note:

Liquid and gas compositions are different!

Px Diagram



Tie line: allows for definition of vapor to liquid ratio, as well as the composition of the vapor and liquid phases

x =
P =
T = -40ºF

Bubble-point curve

Dew-point curve

x (methane)

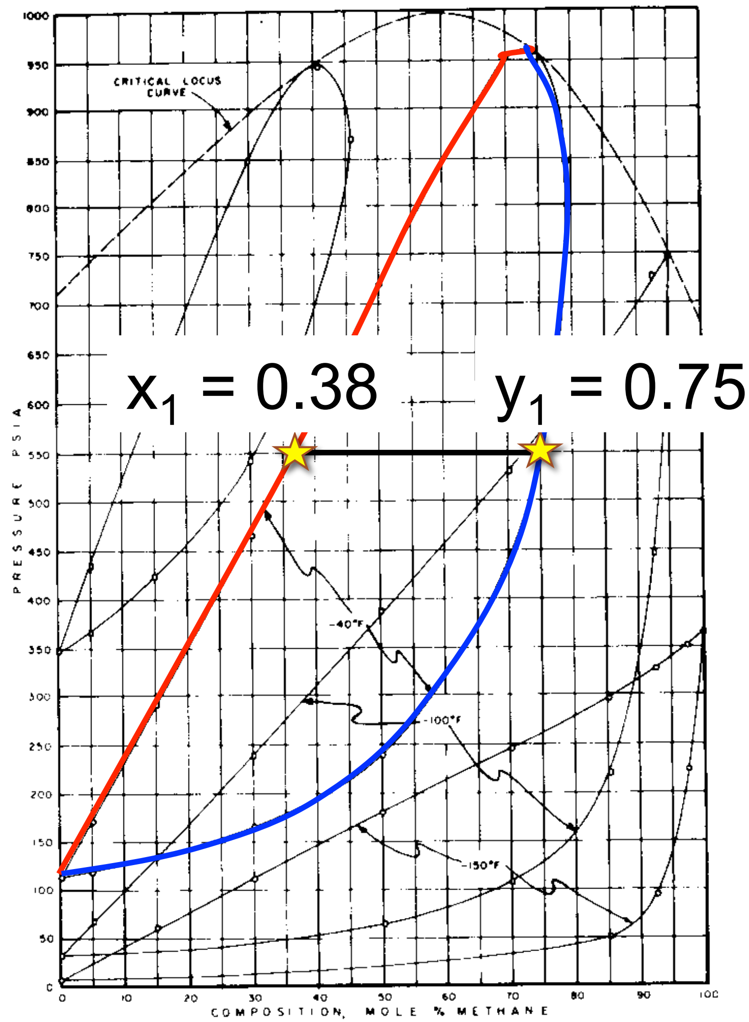
McCain Fig. 2-22

Note:

Liquid and gas compositions are different!

Px Diagram

x = 0.5
P = 500 psia
T = -40ºF



x (methane)

Note:

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McCain Fig. 2-22

Px Diagram

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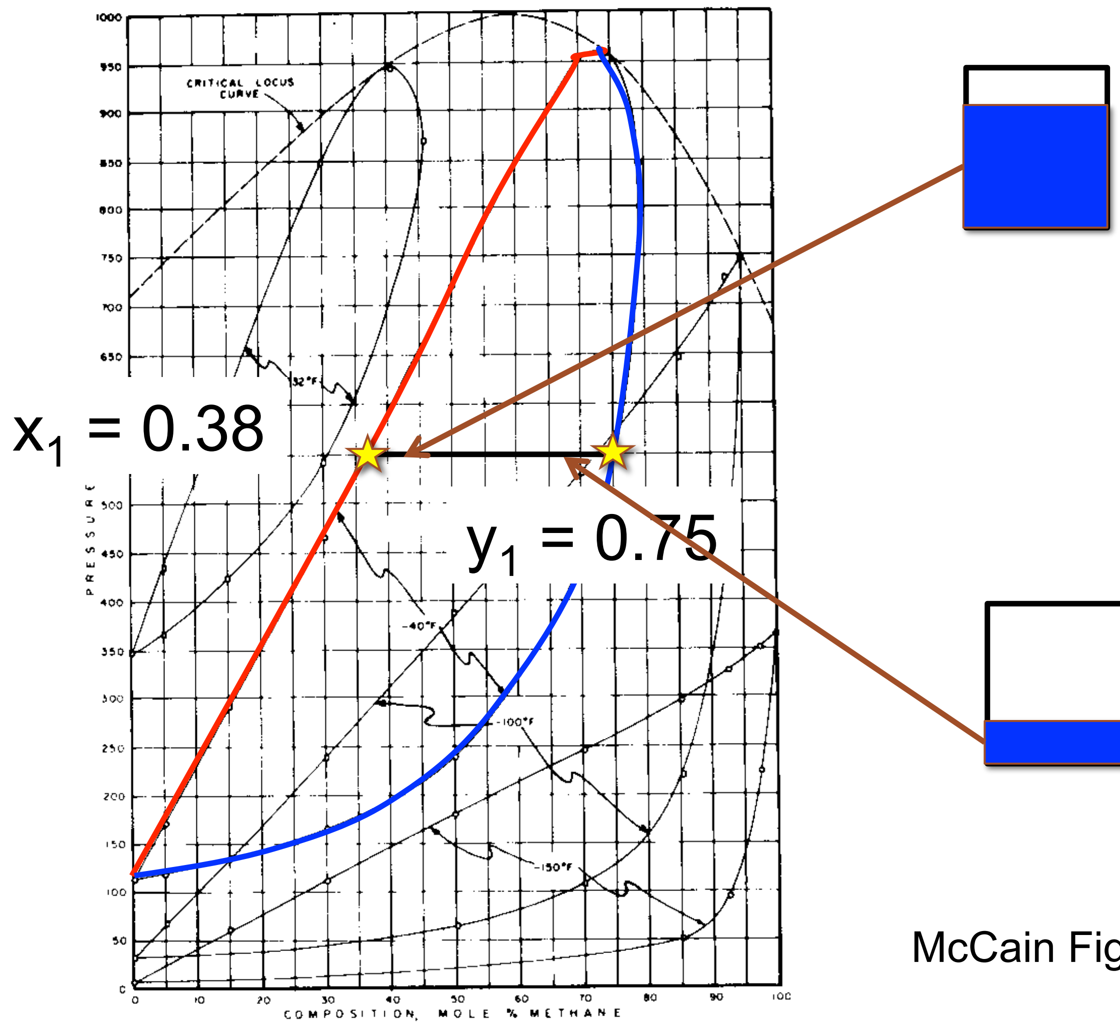

x (methane)

McCain Fig. 2-22

Note:

Liquid and gas compositions are different!

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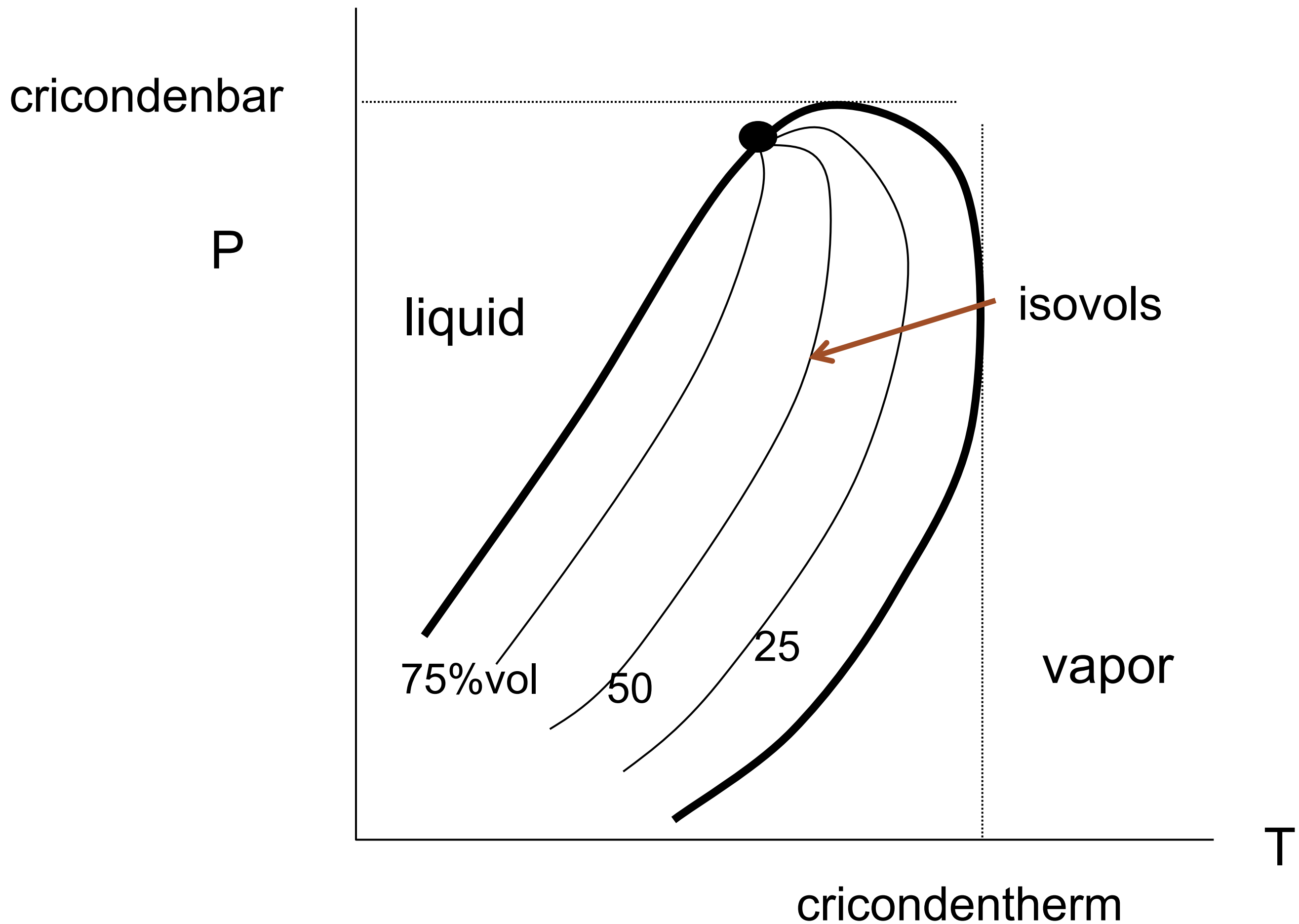
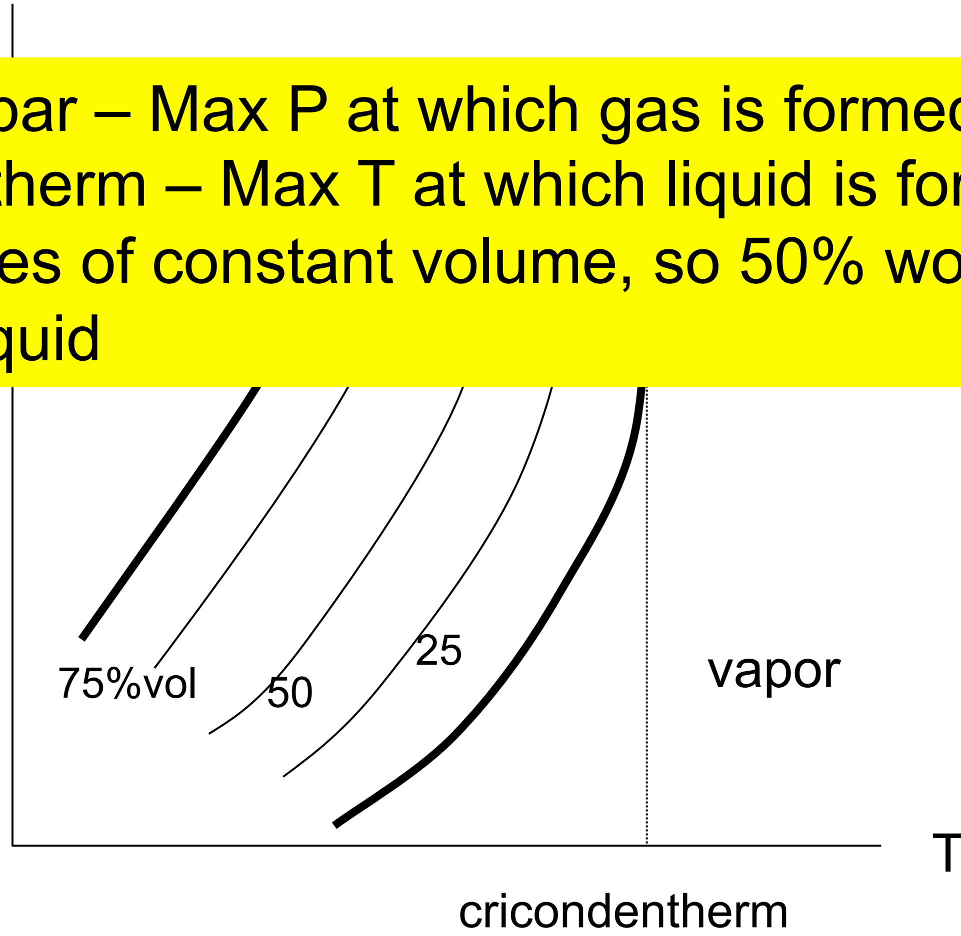
Retrograde Behavior

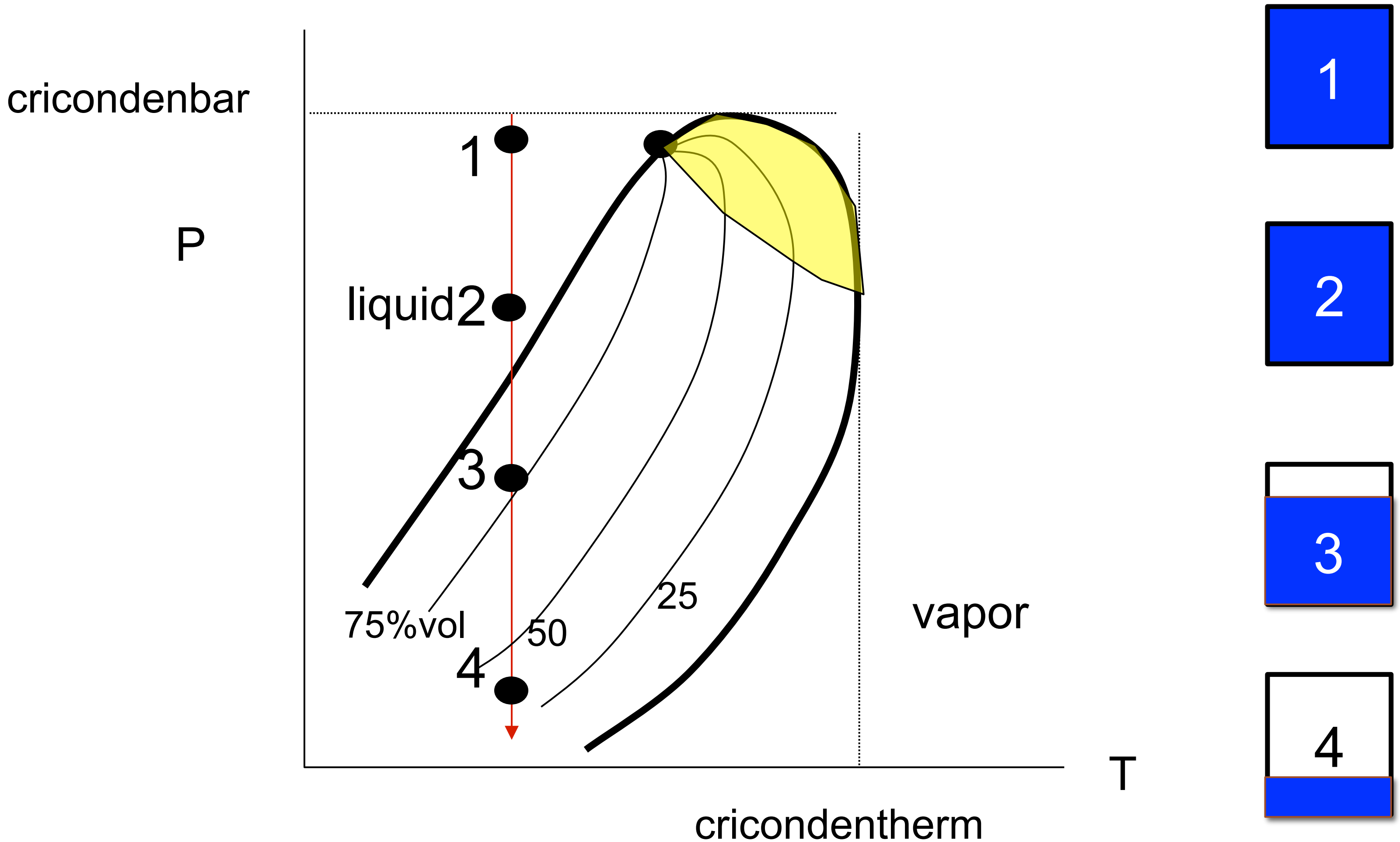


Retrograde Behavior

Cricondenbar – Max P at which gas is formed
Cricondebtherm – Max T at which liquid is formed
Isovol – lines of constant volume, so 50% would be half gas, half liquid



Retrograde Behavior



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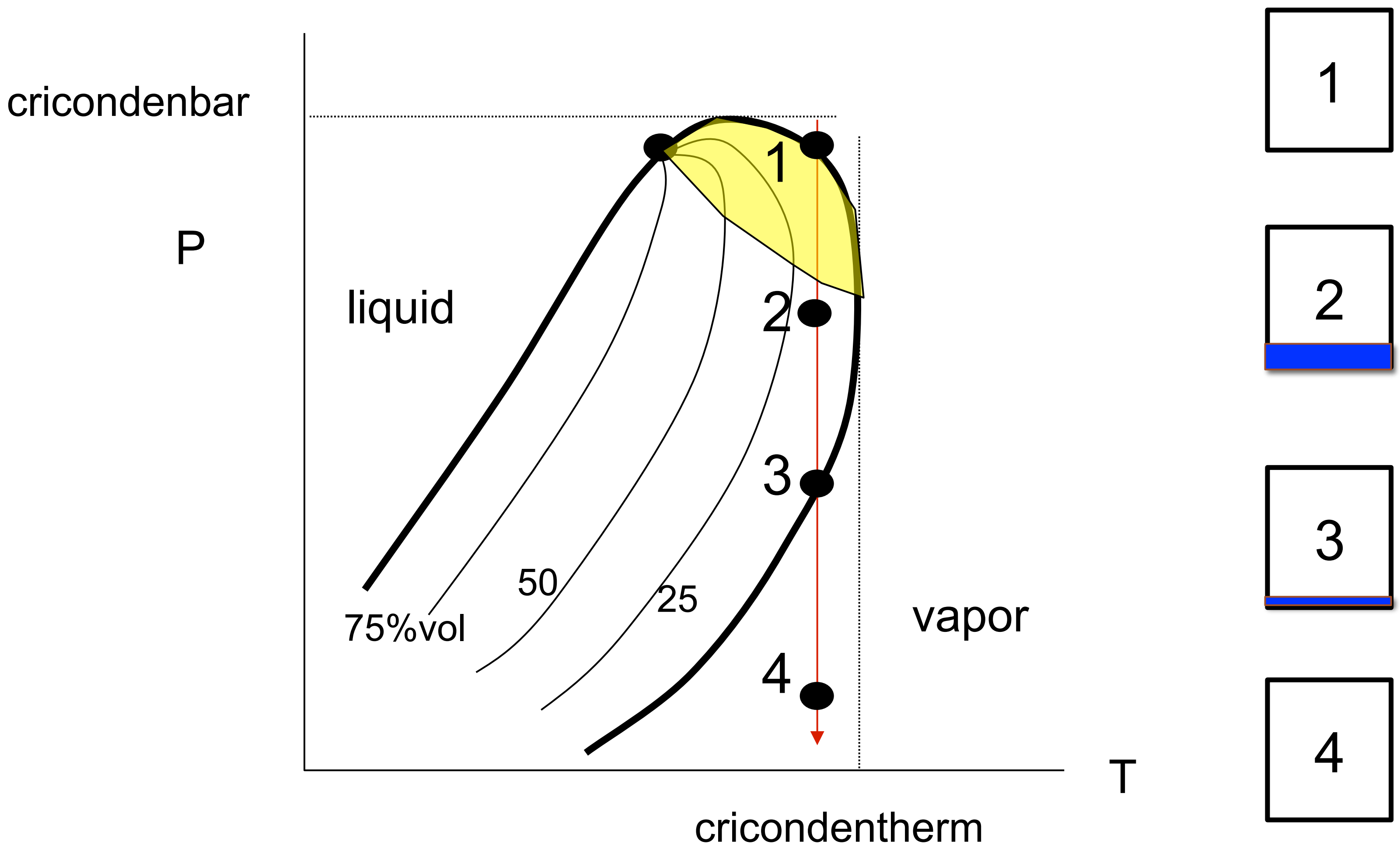
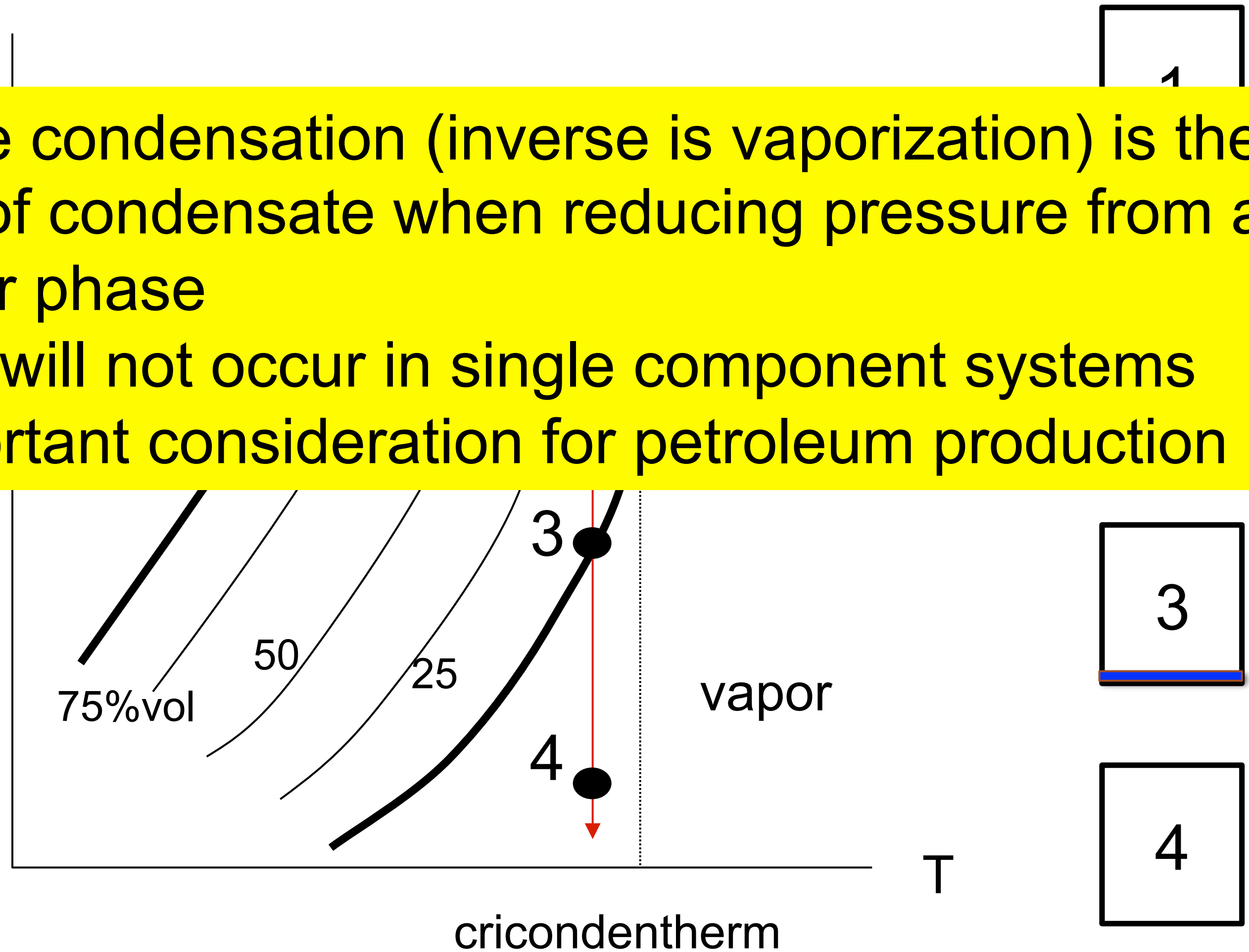


Retrograde Behavior



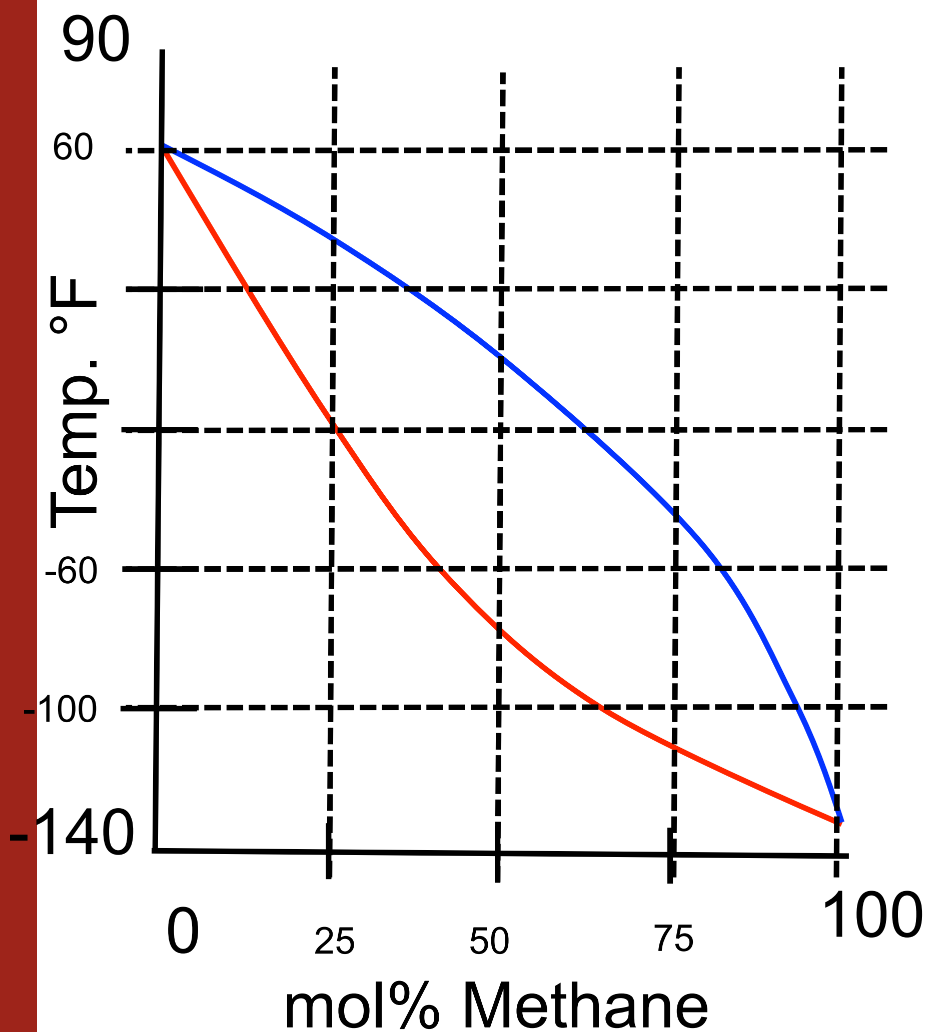
Retrograde condensation (inverse is vaporization) is the formation of condensate when reducing pressure from an initial vapor phase

- This will not occur in single component systems
- Important consideration for petroleum production

Binary and Greater Mixtures

- Bubble-point curve and dew-point curve do not overlap in PT diagram
- Critical point is the point where the dew-point curve and bubble-point curve meet
- Shape and position of PT diagram depends on properties of individual components and composition of mixture
- Counter-intuitive behavior may occur (retrograde behavior). This has consequences for reservoir production!

In-Class Exercise

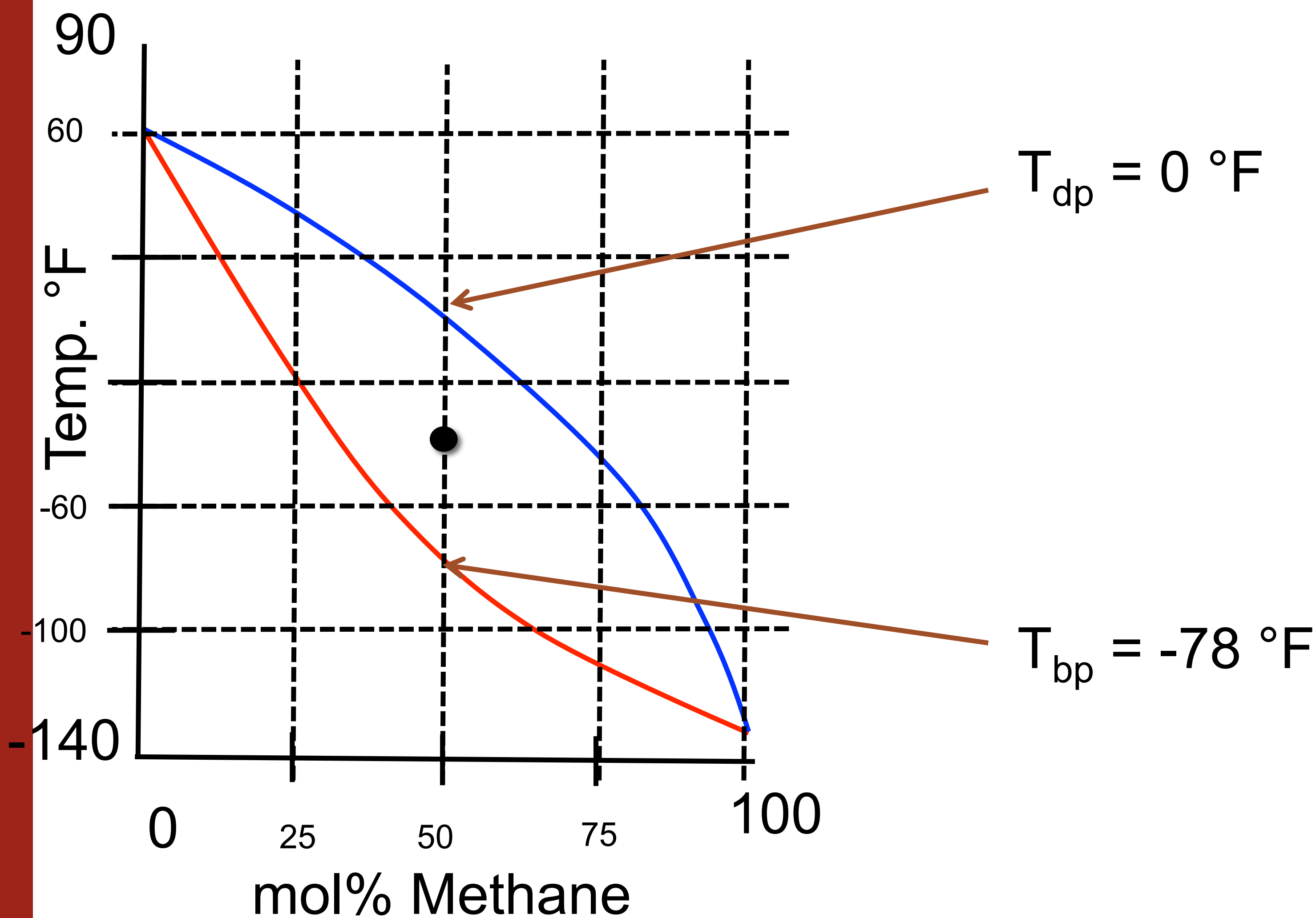


Methane/Ethane @ 500 psi

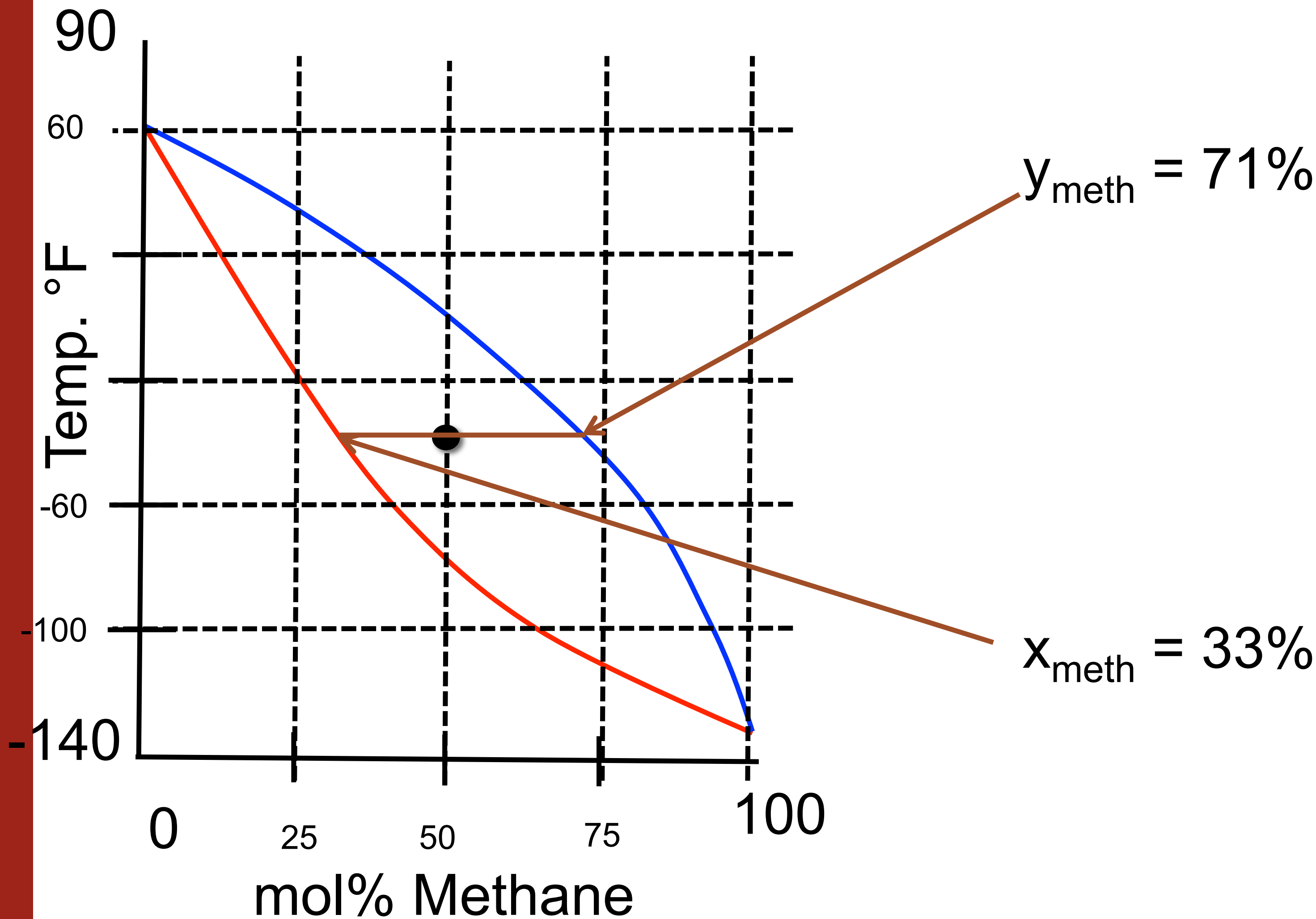
5 moles of 50 mol% methane mixture at -40 °F.

1. What are the bubble and dew point temperatures for this mixture?
2. What is the composition of the liquid and vapor phases?
3. What is the fraction of gas and liquid?

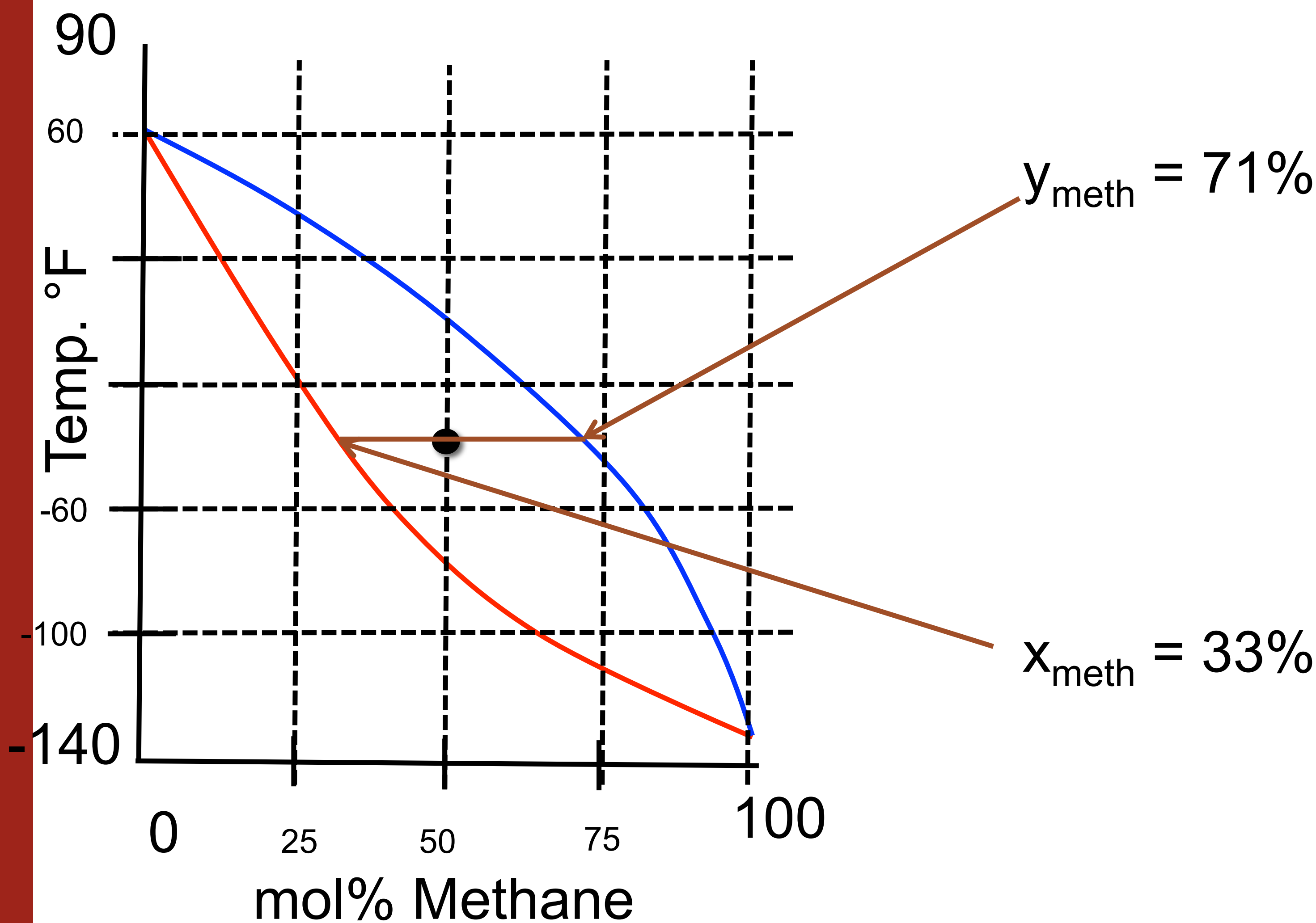
Bubble and Dew Points



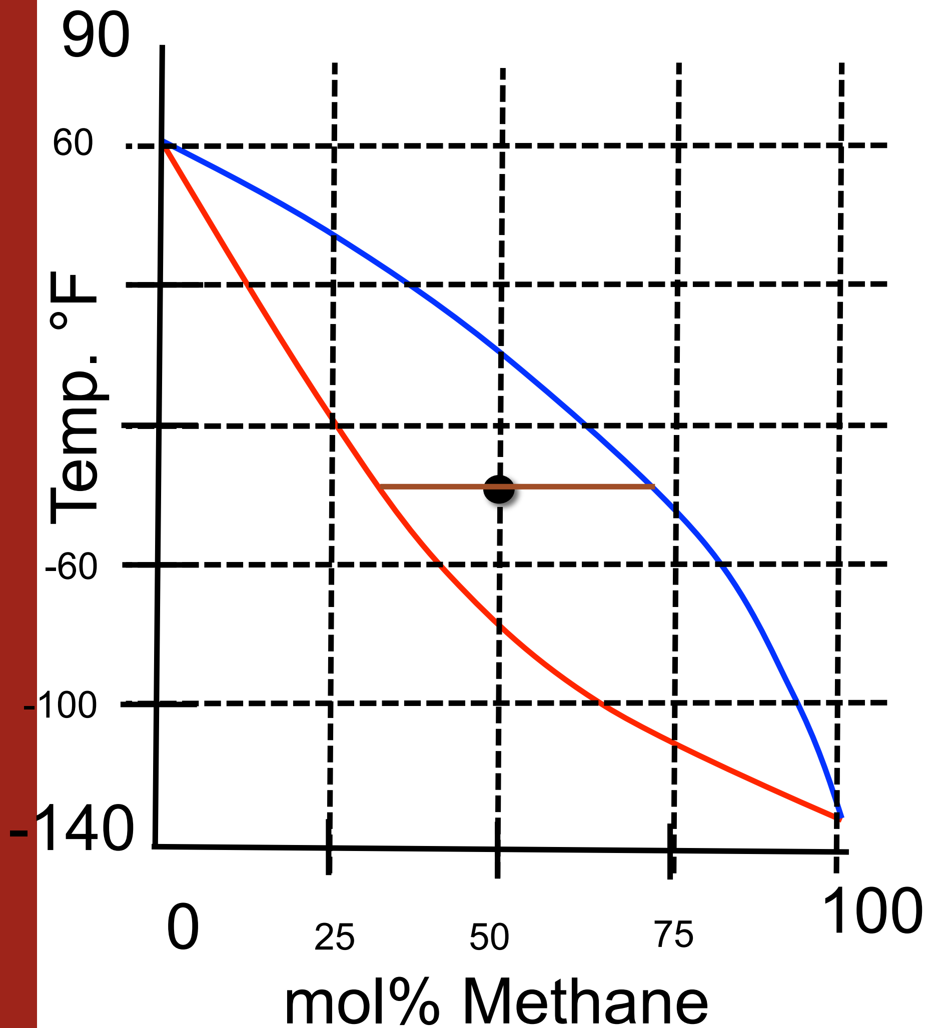
Gas and Liquid Compositions



Gas and Liquid Compositions



Gas and Liquid Fractions



$$M = M_l + M_g$$

$$M_1 = x_1 M_l + y_1 M_g$$

$$M_1 = x_1 M_l + y_1 (M - M_l)$$

$$M_1 = y_1 M + M_l (x_1 - y_1)$$

$$M_l = \frac{M_1 - y_1 M}{x_1 - y_1}$$

$$M_l = \frac{2.5 - 0.71 \times 5}{0.33 - 0.71}$$

$$M_l = 2.76 mol$$