

## Vapor-Liquid Equilibria (VLE)

$$P_{i,L} = P_{i,V} \Rightarrow f_{i,L} = f_{i,V} \Rightarrow \gamma_i x_i f_i(\text{pure liq. } i) = \underbrace{= \varphi_i y_i P}_{\text{"asymmetric" description}}$$

$x_i$ : mole fractions in liq.

$y_i$ : mole fractions in vap.

activities in liq., fugacities in vap.

For low pressures,  $\varphi_i \approx 1$ ;  $f_i(\text{pure}) = P_i^{VP}$

$$\therefore \boxed{y_i P = \gamma_i x_i P_i^{VP}} \quad \text{ideal vapor}$$

Moreover, for ideal liquid mixtures,  $\gamma_i = 1$

$$\Rightarrow y_i P = x_i P_i^{VP} \quad \text{Raoult's Law (very restrictive assumptions)}$$

Example 9.1 VLE of  $\underbrace{n\text{-C}_6}_{\text{comp. 1}} + \underbrace{n\text{-C}_8}_{\text{comp. 2}}$

(2) const.  $T$  at 350 K

$P_1^{VP}(T)$ ,  $P_2^{VP}(T)$  from Antoine Eq.,  
NIST webBook

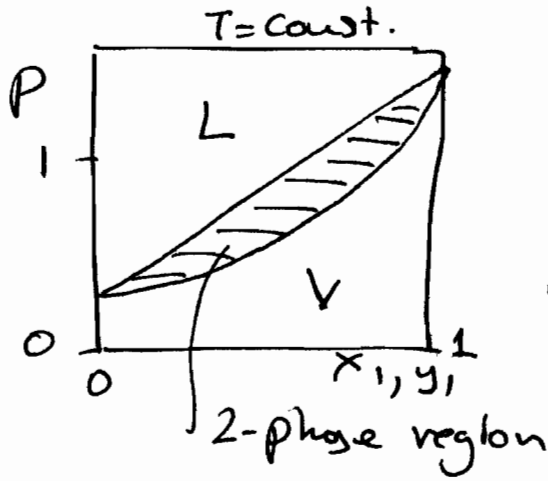
At 350K  $P_1 = 1.3 \text{ bar}$   $P_2 = 0.36 \text{ bar}$  } low enough  
to assume ideal vapor

Hydrocarbons are nonpolar  $\rightarrow$  assume ideal liquid phase

$$P = P_1 + P_2 = x_1 P_1^{VP} + x_2 P_2^{VP}$$

$$y_1 = \frac{P_1}{P} = \frac{x_1 P_1^{VP}}{x_1 P_1^{VP} + x_2 P_2^{VP}}$$

} no iteration needed

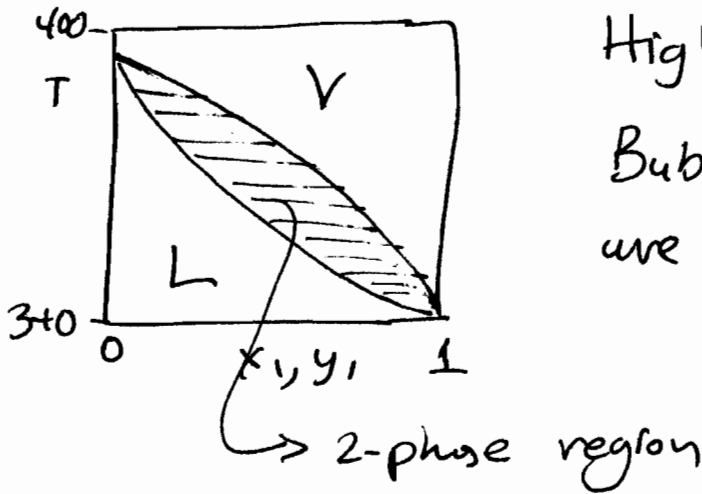


High  $P \rightarrow$  liquid  
 Bubble points on straightline  
 (first bubble in liquid)  
 $\rightarrow$  see calculations in  
 spreadsheet on Book  
 website "Add-ons"

(b) Const  $P$  at  $P=1$  bar

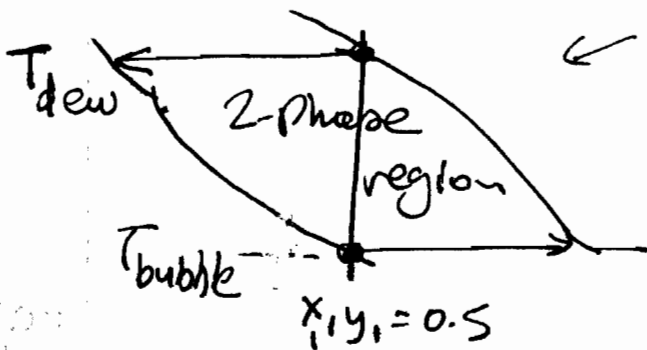
$$x_1 P_1^{VP}(T) + (1-x_1) P_2^{VP}(T) = P$$

non-linear equation given  $x_1 \rightarrow$  compute  $T$   
 $y_1$  as before



High  $T \rightarrow$  vapor  
 Bubble + Dew Point curves  
 are both non-linear

Dew + Bubble points for equimolar system

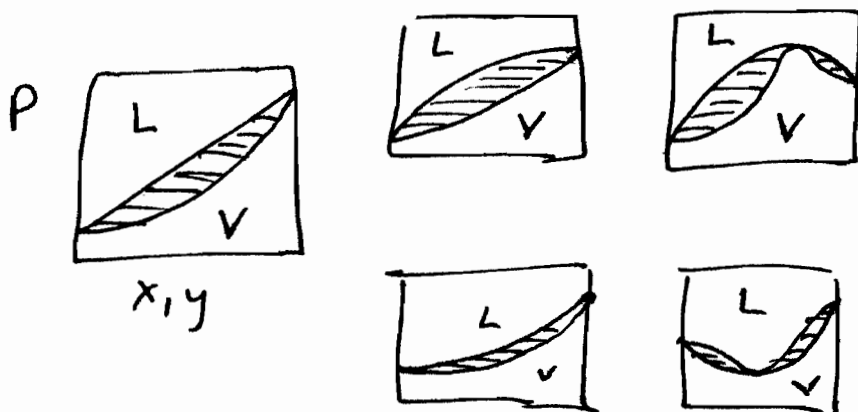


$\leftarrow$  enlargement of region around  
 $x_1, y_1 = 0.5$   
 Iterative calculation!

Non-ideal liquid phase

$$\gamma_i x_i P = y_i P$$

common approach for low-to-moderate pressures



$\gamma_i's > 1$   
positive deviations from Raoult's Law

$\gamma_i's < 1$   
negative deviations from Raoult's Law

Example 9.2

$$\ln \gamma_1 = \frac{C x_2^2}{RT} \quad \ln \gamma_2 = \frac{C x_1^2}{RT}$$

Margules 1-constant  
 $P_1^{VP} = 1 \text{ bar}$   $P_2^{VP} = 2 \text{ bar}$

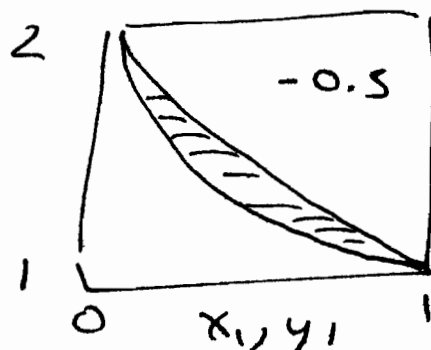
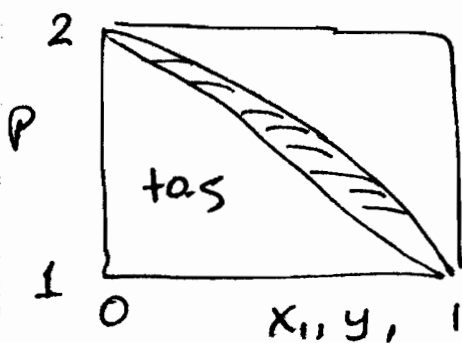
(a)  $C/RT = +0.5$

(b)  $C/RT = -0.5$

$$P = P_1 + P_2 = x_1 \gamma_1 P_1^{VP} + x_2 \gamma_2 P_2^{VP}$$

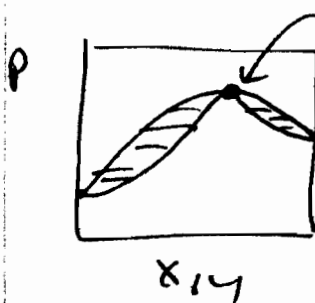
$$y_1 = \frac{P_1}{P} = \frac{x_1 \gamma_1 P_1^{VP}}{x_1 \gamma_1 P_1^{VP} + x_2 \gamma_2 P_2^{VP}}$$

non-iterative calculation



## Azeotropy

For sufficiently strong non-ideality, or for components of similar vapor pressures,



azeotropic point

$$x_1 = y_1$$

$$x_2 = y_2$$

$$\delta_1 y_1 P_i^{vp} = y_1 P \Rightarrow$$

$$\delta_1 = P / P_i^{vp}$$

$$\text{Similarly, } \delta_2 = P / P_2^{vp}$$

[For positive deviations from Raoult's Law]

## Thermodynamic consistency tests

Given measurements of  $\{x_i\}$ ,  $\{y_i\}$ ,  $\{P\}$  for VLE, the activity coefficients can be obtained from

$$\delta_i = \frac{y_i P}{x_i P_i^{vp}} \quad \text{as functions of composition}$$

from Gibbs-Duhem @ const  $T, P$

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0 \Rightarrow$$

(no proof)

$$\int_0^1 \ln \frac{\delta_2}{\delta_1} dx_1 = 0$$