

CE407 SEPARATIONS

Lecture 04

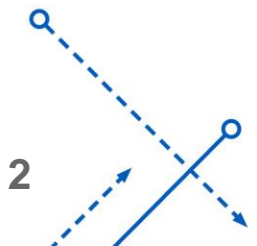
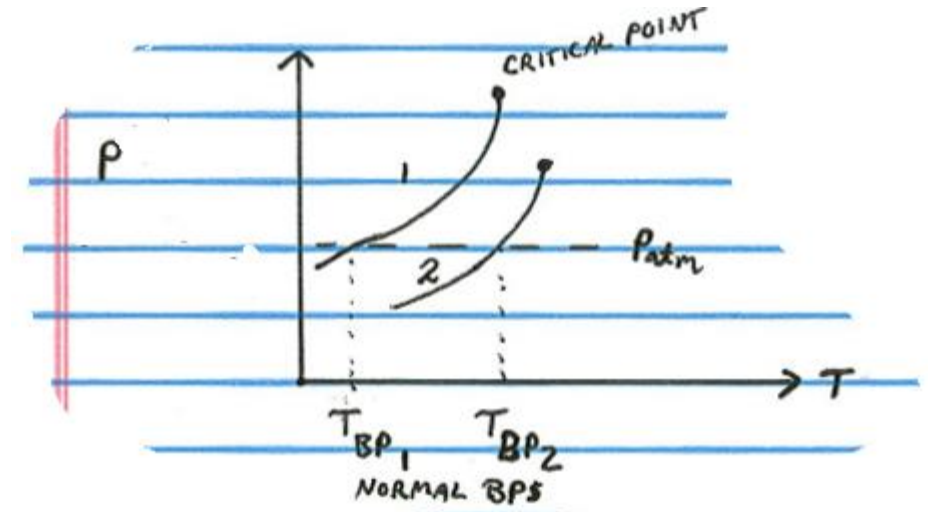
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Distillation

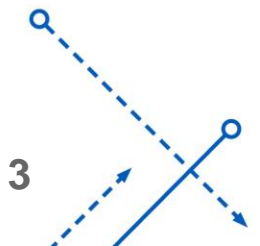
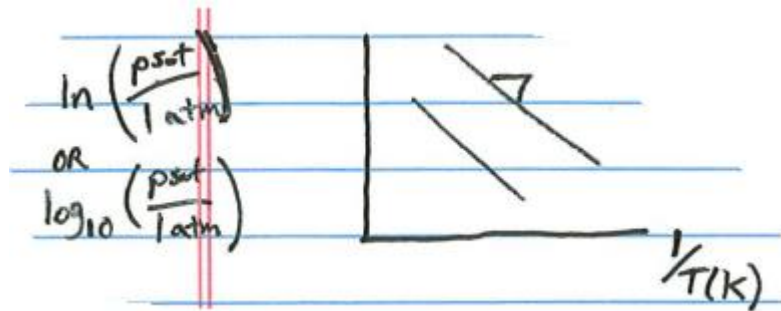
- Whereby a mixture of chemicals is separated by exploiting differences in boiling points
- This lecture deals with thermodynamic background material relevant to this topic
- **Vapor Pressure, P^{sat}**
 - P^{sat} is very non-linear
 - P^{sat} is very sensitive to temperature
- Component 1 is more volatile than component 2
 - At any given pressure component 1 boils at a lower temperature than component 2
 - At any given temperature component 1 has a higher vapor pressure than component 2



Clausius Clapeyron Equation

$$\ln P^{sat} = \frac{-\Delta H^{vap}}{R} \frac{1}{T} + \text{constant}$$

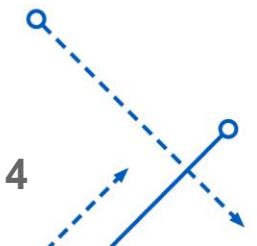
- P^{sat} is vapor pressure
- $-\Delta H^{vap}$ is Heat of Vaporization
- R is the gas constant
- T is Absolute Temperature
- Vapor pressure is linearized versus $1/T$, but is not perfectly linear
 - $-\Delta H^{vap}$ is Heat of Vaporization is not a constant



Antoine Equation

$$\log \left(\frac{p^{sat}}{1 \text{ atm}} \right) = A - \frac{B}{T + C}$$

- Antoine coefficients A, B, and C are available in many resources
 - For this course use the values from the course website, which can be found in the code in the CODE tab
- Make sure your use of the equation is in agreement with the source regarding the following:
 - Natural logarithm versus Base 10 logarithm
 - Pressure and Temperature Units (temperature MUST be in the same scale as the coefficients were determined with)
 - Applicable temperature range
- If interpolating values from a table of vapor pressure versus temperature: convert to $\ln(P^{sat})$ (or $\log_{10} p^{sat}$) and $1/T$ to do an linear interpolation



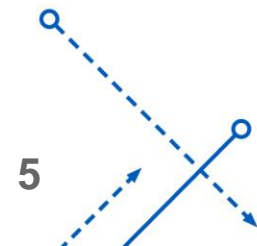
Vapor Liquid Equilibrium (VLE)



- At equilibrium, the values of x_i and y_i for each component are set by temperature and pressure
- The overall composition will determine the relative amount of vapor versus liquid phases

- Distribution Coefficient (k factor) $k_i = \frac{y_i}{x_i}$

- Relative Volatility $\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{k_i}{k_j}$



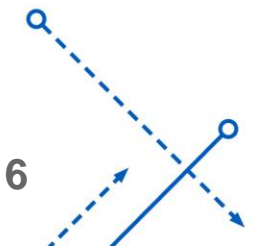
Binary Systems VLE

- For a binary system \mathbf{x} and \mathbf{y} refer to the light (more volatile) component and do not require a subscript

- Light Component $k_1 = y_1/x_1 = \frac{y}{x}$

- Heavy Component $k_2 = y_2/x_2 = \frac{(1-y)}{(1-x)}$

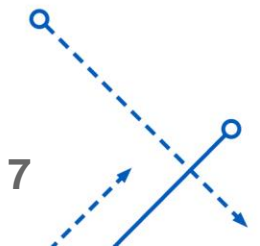
$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{y/x}{(1-y)/(1-x)}$$



Raoult's Law

$$y_i P = x_i P_i^{sat}(T)$$

- Requirements
 - Ideal Gas Behavior
 - Distillation takes place at high temperatures and moderate to low pressures so this is a VERY good assumption
 - Ideal Liquid Mixture
 - Components need to have similar structures so that they are not interacting
 - This is a good assumption in refining processes
 - When water is present this is NOT necessarily a good assumption



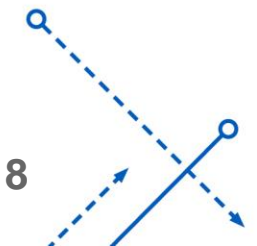
Raoult's Law, continued

- Now
$$\frac{y_i}{x_i} = k_i(T, P) = \frac{P_i^{sat}(T)}{P}$$
- When Raoult's Law applies $\alpha_{ij} \approx \textit{constant}$ with respect to temperature

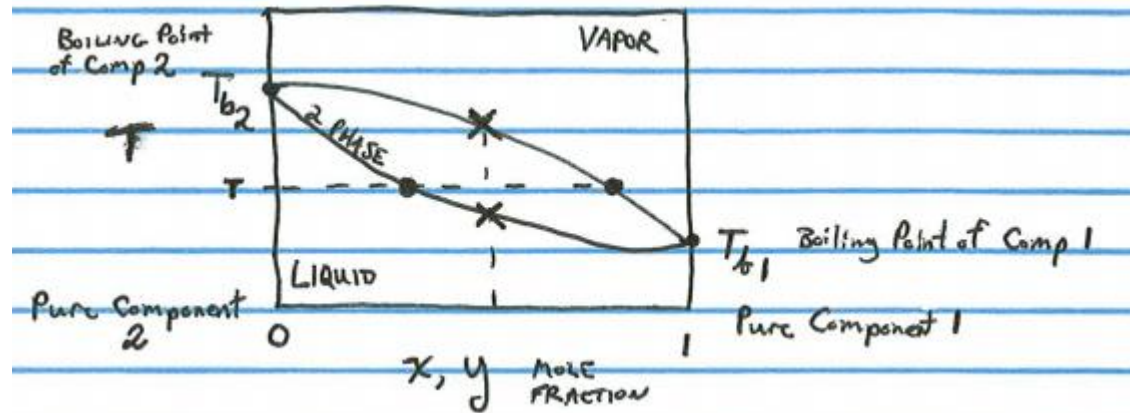
$$\alpha_{ij} = \frac{P_i^{sat}(T)}{P_j^{sat}(T)}$$

$$y = \frac{\alpha}{1 + (\alpha - 1)x}$$

- Which is a rearrangement of
$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{y/x}{(1-y)/(1-x)}$$
- One can calculate α_{ij} at the boiling point of each component and then take average

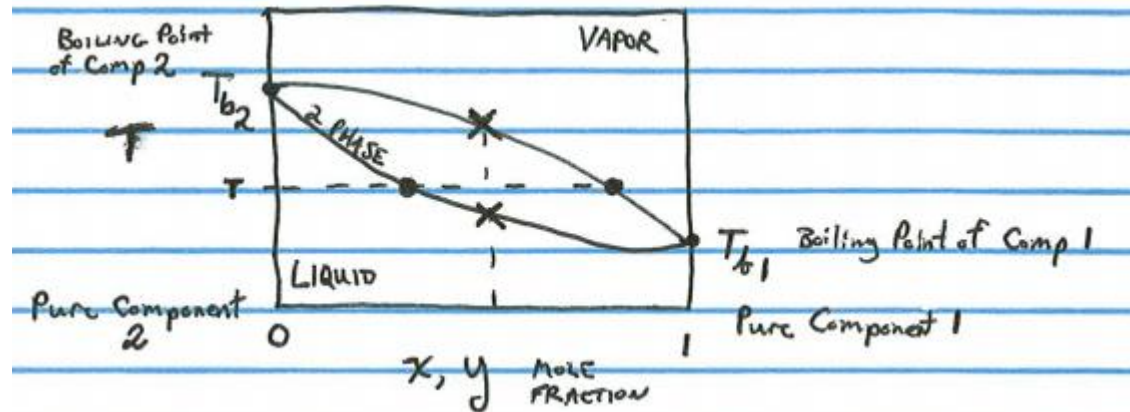


Binary T_{xy} Diagram



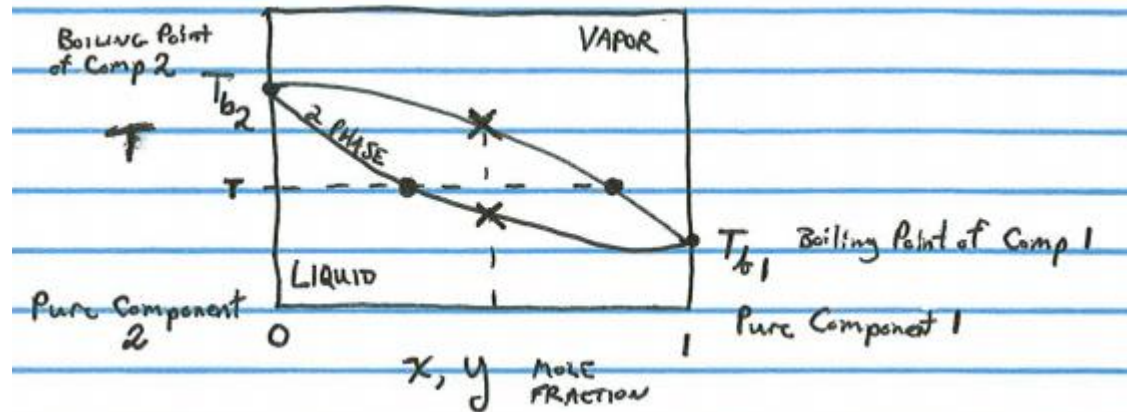
- Below the two phase bubble: One phase, Liquid
- Above the two phase bubble: One phase, Vapor
- Within the two phase bubble: Both phases are present
- Below the bubble – abscissa refers to x
- Above the bubble – abscissa refers to y

Binary T_{xy} Diagram



- Within the bubble
 - Locate the point for the overall combined mixture
 - Abscissa is the overall mole fraction (both phases accounted for)
 - Ordinate is the temperature
 - Follow constant temperature to each curve of bubble (indicated above by dot)
 - Value of abscissa on lower curve is equilibrium mole fraction in liquid phase, x
 - Value of abscissa on upper curve is equilibrium mole fraction in vapor phase, y

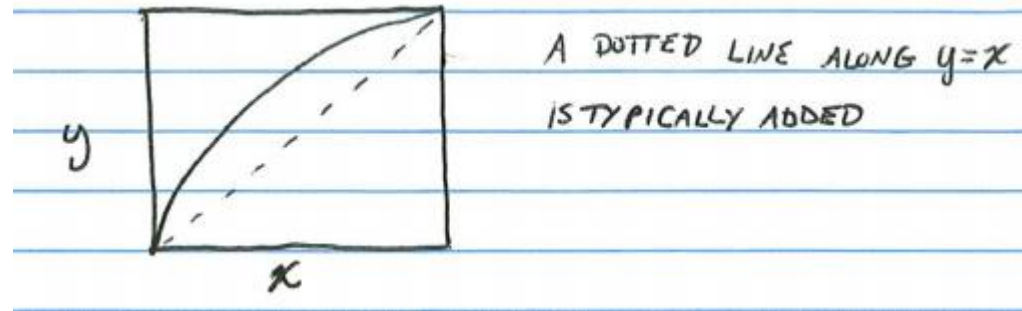
Binary T_{xy} Diagram



- x and y refer to the mole fractions of component 1
 - The more volatile, i.e. Lower Boiling Point Component
- Point marked with X on upper curve is the **DEW POINT** for vapor at that mole fraction y
 - Composition of first drop of liquid is found by value of x located on lower curve at the same temperature
- Point marked with X on lower curve is the **BUBBLE POINT** for liquid at that mole fraction x
 - Composition of first bubble formed is found by value of y located on upper curve at the same temperature

Vapor Liquid Equilibria (VLE) Curve

- If one plots the value of y versus the value of x that it is in equilibrium with, the following graphs results



- Note that each x and y pair are the values on upper and lower curves at a given temperature on the T_{xy} diagram
- Actual data is always preferable to calculated data
- Having said that, let's look at a method to calculate the VLE equilibria curve!

VLE Curve, continued

- Add up the Raoult's Law expression for each component

$$y_1 P = x_1 P_1^{sat}(T) \quad \text{component 1}$$

$$y_2 P = x_2 P_2^{sat}(T) \quad \text{component 2}$$

$$(y_1 + y_2) P = x_1 P_1^{sat}(T) + x_2 P_2^{sat}(T) \quad \text{sum}$$

- Rearrange the equation, noting that $(y_1 + y_2) = 1$
 - Replace x_1 with x and x_2 with $(1-x)$

$$x = \frac{P - P_2^{sat}(T)}{P_1^{sat}(T) - P_2^{sat}(T)}$$

$$y = \frac{x P_1^{sat}(T)}{P}$$



VLE Curve, continued

- Use the Antoine Relationship to calculate values of $P_1^{\text{sat}}(T)$ and $P_2^{\text{sat}}(T)$ at various temperatures
- Use those values of $P_1^{\text{sat}}(T)$ and $P_2^{\text{sat}}(T)$ to calculate x and y equilibrium values for each temperature

T	x	y
T_{b1}	0	0
⋮	⋮	⋮
T_{b2}	1	1

- Plot
 - T versus x and T versus y on the same graph to generate T_{xy} diagram
 - y versus x to generate **VLE** curve

