

CE407 SEPARATIONS

Lecture 08

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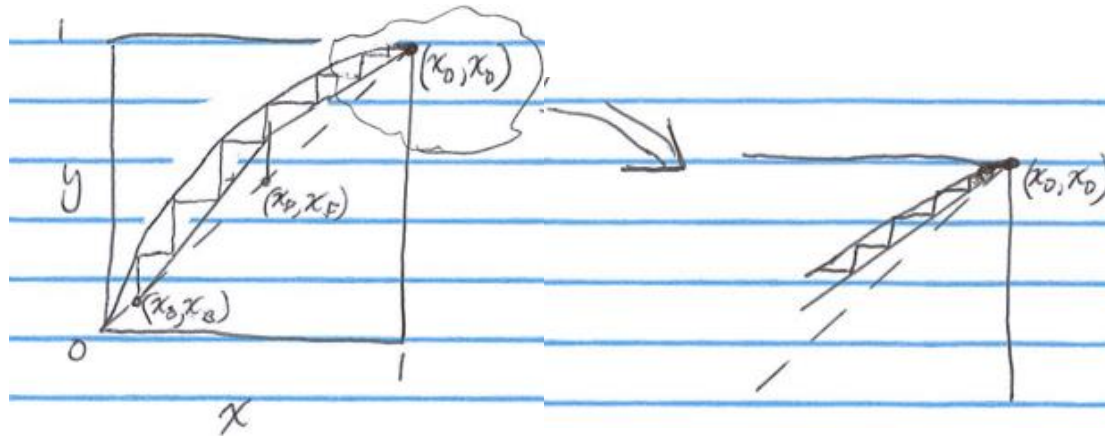
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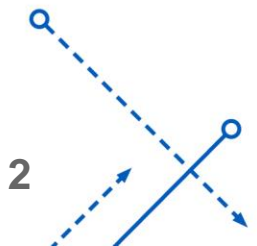
Continuous Distillation with Reflux – Nearly Pure Products

McSH pp 692-694

- What if the purity required is $x_D = 0.9999$?

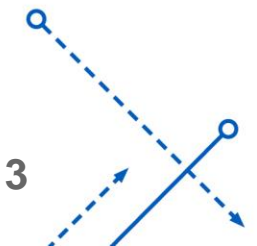


- You simply cannot draw the triangle small enough
- Not even if you blow up the section near x_D
- What if the purity required is $x_D = 0.999999$?
 - The width of your pen stroke doesn't allow you to distinguish between $x_D = 0.9999$ and $x_D = 0.999999$



What to do for Very High Purity cases?

- In a region a short distance from $x_D = 0.9999$ the equilibrium curve is fairly straight and α is approximately constant
- According to constant molal overflow assumption, the Operating Line is straight
- Those are the two assumptions of the **Kremser Equation!!!**
- We cannot use the Kremser Equation across the entire column because the EQ Curve has so much curvature
- We cannot use the McCabe-Thiele method across the entire column because the EQ Curve and the OP Line converge so closely that the steps become too small as we approach x_D values extremely close to 1
- We will split the column into two sections with a cutoff value of x , x_{cutoff}
- x_{cutoff} is chosen so that we can successfully use McCabe-Thiele below the cutoff (i.e. the triangles are not too small) and that the EQ curve can be considered straight between x_{cutoff} and x_D so that Kremser is appropriate



Kremser Region

Equilibrium “Line”

- We need to approximate the EQ Curve with a straight line in this region
- Obviously the (1, 1) must be on the EQ Line
- We need one more point to define the EQ Line
 - $y^* = y^*(x_{\text{cutoff}})$
- In other words , use VLE data or relationship to calculate what value of y is in equilibrium with x_{cutoff}
 - Note that in Excel one can use Goalseek to find the temperature leading to $x = x_{\text{cutoff}}$ and then read off $y^* = y^*(x_{\text{cutoff}})$
- Solve for $y = mx + b$ that satisfies both (1, 1) and $(x_{\text{cutoff}}, y^*(x_{\text{cutoff}}))$

Operating Line

- We already have that from
$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}$$

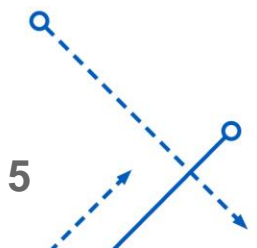
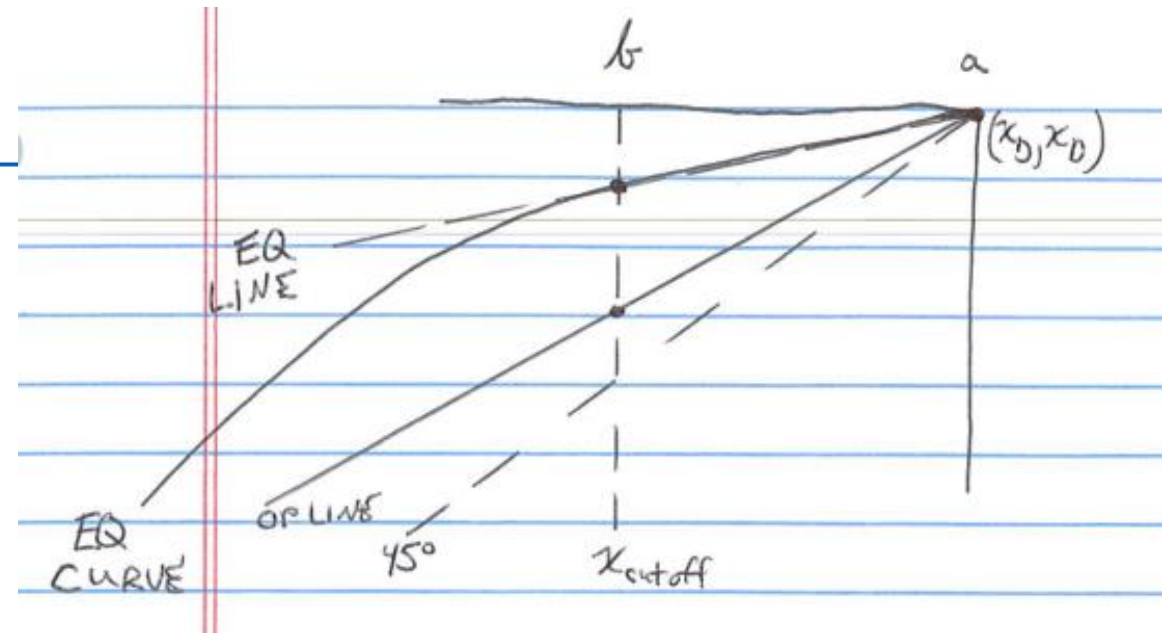
Caution: We are trying to determine a mole fraction that has many significant digits

- Carry several more digits in each term of the calculation than the number in the specification



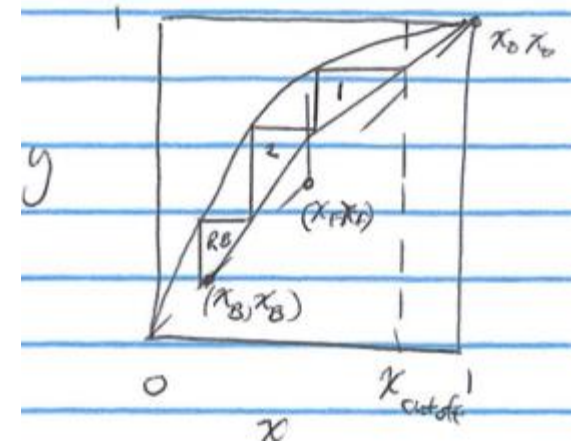
High Purity – Kremser Section

- Kremser Equation
$$N = \frac{\ln[(y_b - y_b^*) / (y_a - y_a^*)]}{\ln[(y_b - y_a) / (y_b^* - y_a^*)]}$$
- a is at $x = x_D$
 - $x_a = x_D$
 - $y_a = x_D$
 - $y_a^* = y^*(x_D)$ is calculated from the the EQ “Line” $y = m * x_D + b$
 - Note that the “b” has nothing to do with position b, it is the intercept in the EQ “Line” equation
- b is at $x = x_{cutoff}$
 - $x_b = x_{cutoff}$
 - $y_b = \frac{R}{R+1} x_{cutoff} + \frac{x_D}{R+1}$
 - $y_b^* = y^*(x_{cutoff})$ is the value of y in equilibrium with x_{cutoff} . This is the value that we used to determine the EQ “Line”. You could calculate it with the EQ “Line” equation, but why bother? You already have it.



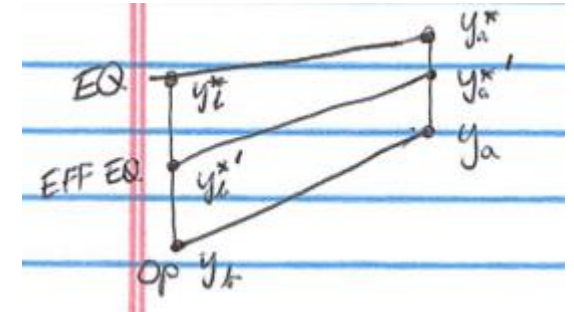
High Purity

- Plug the values for y_a , y_b , y_a^* , and y_b^* into Kremser equation to obtain N_{Kremser}
- Use McCabe-Thiele to determine the number of stages between x_B and x_{cutoff}
- This gives you $N_{\text{graphical}}$
 - In the graph at the right, $N_{\text{graphical}} = 2 + \text{Reboiler}$
- $N = N_{\text{Kremser}} + N_{\text{graphical}}$
- As always, round up for partial stages



High Purity with Non-ideal Stages

- We need to calculate effective equilibrium values for y_a^* and y_b^*
- $y_a^{*'} = y_a + \eta_M(y_a^* - y_a)$
- $y_b^{*'} = y_b + \eta_M(y_b^* - y_b)$
- $$N = \frac{\ln[(y_b - y_b^{*'}) / (y_a - y_a^{*'})]}{\ln[(y_b - y_a) / (y_b^{*'} - y_a^{*'})]}$$
- Do the same procedure used before for McCabe-Thiele and η_M to determine $N_{\text{graphical}}$

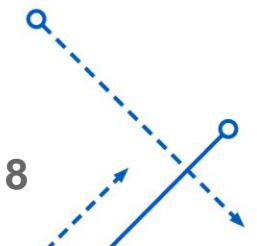


Enthalpy Balances McSH pp 694-701 (also Eq. 21-1 and 21.2 on pp 679 and 682)

- We want to develop expressions for

$$\begin{array}{ccc}
 H_x(T, x) & \text{and} & H_y(T, y) \\
 \text{Liquid Enthalpy} & & \text{Vapor Enthalpy}
 \end{array}$$

- We will determine enthalpy as a function of temperature, composition and phase
- Enthalpy is a state function and is relative to a reference state. We can choose any state as our zero point – units are energy/mole
 - We will choose to use: Each pure component as a liquid at the boiling temperature of the lighter component – *this choice will prove to simplify later calculations...*
- Declare: $H_{x,1}(T_{nb1}) = 0$ and $H_{x,2}(T_{nb1}) = 0$
- $H_{x,1}$ is the enthalpy of pure component 1, liquid form
- $H_{x,2}$ is the enthalpy of pure component 2, liquid form
- T_{nb1} is the Normal Boiling Temperature of pure Component 1
- T_{nb2} is the Normal Boiling Temperature of pure Component 2



Enthalpy of Pure Liquids

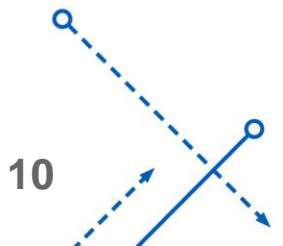
- $H_{xi}(T)$ is the enthalpy of pure component i in liquid form at temperature T
- $H_{xi}(T) = H_{xi}(T_{nb1}) + C_{pi}^L * (T - T_{nb1})$
 - C_{pi}^L is the Liquid Heat Capacity of Pure Component i
 - This assumes a constant value for the heat capacity
 - Units are $\frac{\text{energy}}{\text{mol } ^\circ\text{C}}$ eg $\frac{\text{cal}}{\text{mol } ^\circ\text{C}}$
 - Because we have chosen a reference of $H_{xi}(T_{nb1}) = 0$

$$H_{xi}(T) = C_{pi}^L * (T - T_{nb1})$$

Enthalpy of Pure Vapors, light component

- $H_{y1}(T)$ is the enthalpy of pure component 1 in vapor form at temperature T
- $H_{y1}(T) = H_{x1}(T_{nb1}) + \Delta H_1^{vap}(T_{nb1}) + C_{p1}^V * (T - T_{nb1})$
 - C_{p1}^V is the Vapor Heat Capacity of Pure Component 1
 - This assumes a constant value for the heat capacity
 - Units are $\frac{\text{energy}}{\text{mol } ^\circ\text{C}}$ eg $\frac{\text{cal}}{\text{mol } ^\circ\text{C}}$
 - $\Delta H_1^{vap}(T_{nb1})$ is the heat of vaporization of pure component 1 at its normal boiling temperature
 - Because we have chosen a reference of $H_{xi}(T_{nb1}) = 0$

$$H_{y1}(T) = \Delta H_1^{vap}(T_{nb1}) + C_{p1}^V * (T - T_{nb1})$$



Enthalpy of Pure Vapors, heavy component

- $H_{y2}(T)$ is the enthalpy of pure component **2** in vapor form at temperature T

- $$H_{y2}(T) = H_{x2}(T_{nb1}) + C_{p2}^L * (T_{nb2} - T_{nb1}) + \Delta H_2^{vap}(T_{nb2}) + C_{p2}^V * (T - T_{nb2})$$

reference state raise liquid temp to T_{nb2} convert to vapor at T_{nb2} superheat vapor to final temp

- $\Delta H_2^{vap}(T_{nb2})$ is the heat of vaporization of pure component 2 at its normal boiling temperature

- It will prove useful to express $C_{p2}^V * (T - T_{nb2})$ as

$$\begin{aligned}
 C_{p2}^V * (T - T_{nb2}) &= C_{p2}^V * (T - T_{nb1} + T_{nb1} - T_{nb2}) \\
 &= C_{p2}^V * (T_{nb1} - T_{nb2}) + C_{p2}^V * (T - T_{nb1})
 \end{aligned}$$

- This allows all four terms (H_{x1} , H_{x2} , H_{y1} , H_{y2}) to be expressed in terms of $(T - T_{nb1})$
- Because we have chosen a reference of $H_{xi}(T_{nb1}) = 0$

$$H_{y2}(T) = C_{p2}^L * (T_{nb2} - T_{nb1}) + \Delta H_2^{vap}(T_{nb2}) + C_{p2}^V * (T_{nb1} - T_{nb2}) + C_{p2}^V * (T - T_{nb1})$$

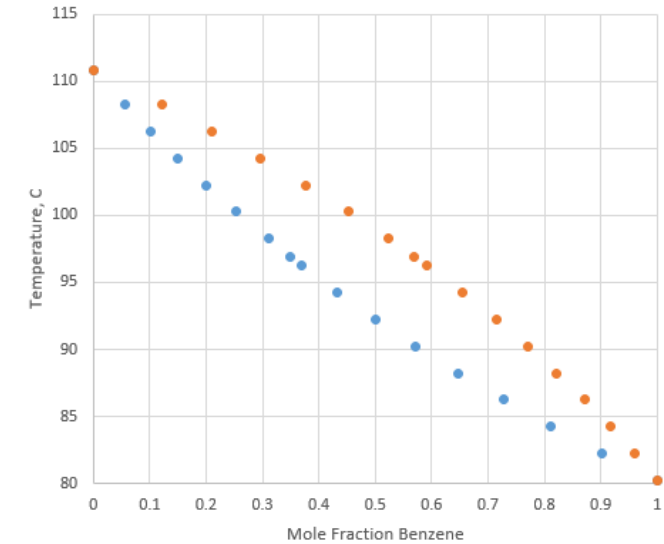
Example

- Benzene (1) and Toluene (2)

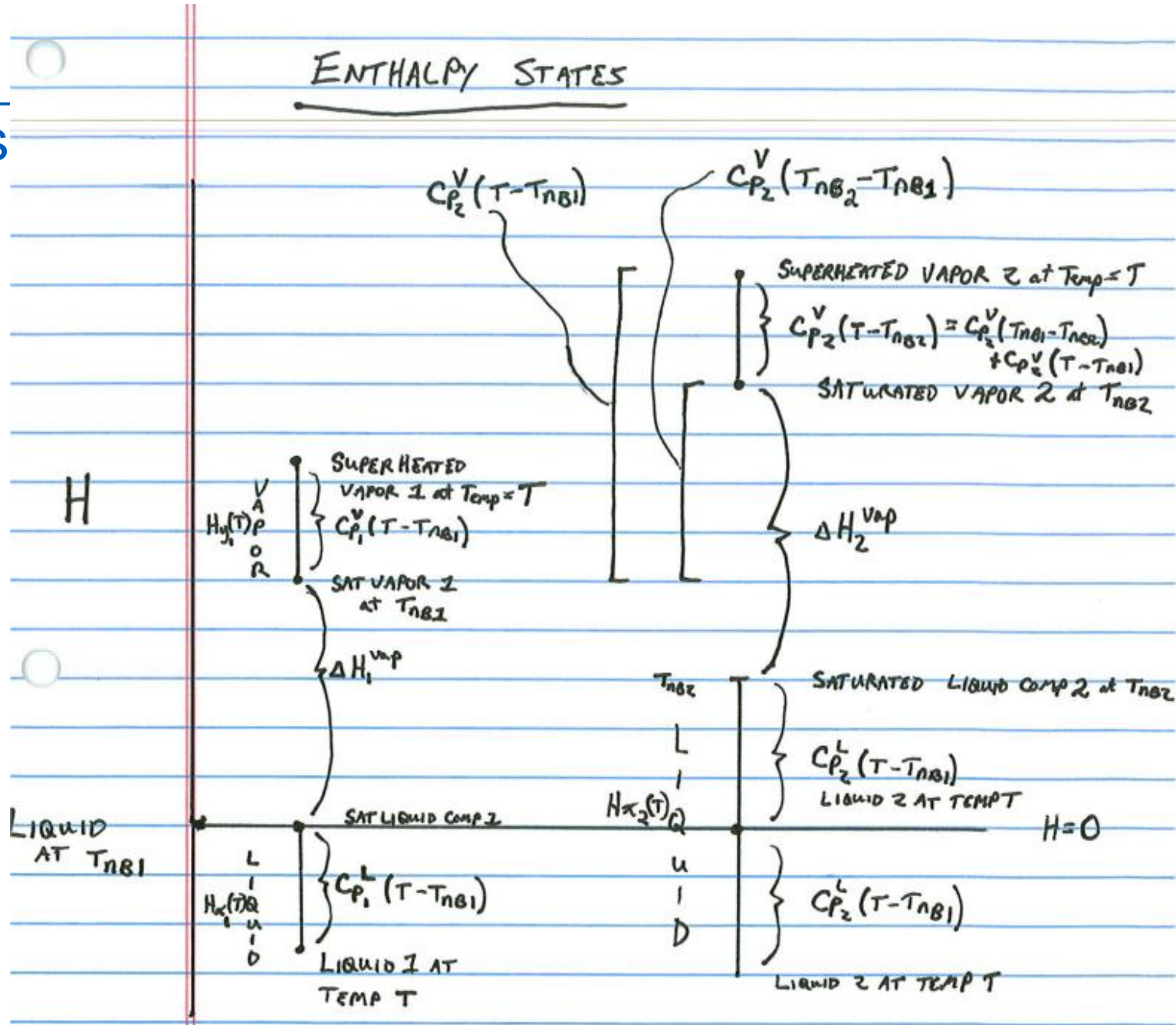
| Component | C_{pi}^L cal/molC | C_{pi}^V cal/molC | ΔH_i^{vap} cal/mol | T_{nbi} C |
|-----------|---------------------|---------------------|----------------------------|-------------|
| 1 | 33 | 23 | 7360 | 80.1 |
| 2 | 40 | 33' | 7960 | 110.6 |

- $H_{x1}(T) = 0 + 33 * (T - 80.1) = 33 * (T - 80.1)$
- $H_{x2}(T) = 0 + 40 * (T - 80.1) = 40 * (T - 80.1)$
- $H_{y1}(T) = 0 + 7360 + 23 * (T - 80.1) = 7360 + 23 * (T - 80.1)$
- $H_{y2}(T) = 0 + 40 * (110.6 - 80.1) + 7960 + 33' * (80.1 - 110.6) + 33' * (T - 80.1)$
 $= 8174 + 33' * (T - 80.1)$

Txy Phase Diagram
Benzene and Toluene
Atmospheric Pressure



Enthalpy States



Enthalpy of Mixtures

- Liquid Mixtures
 - $H_x(T, x) = x * H_{x1}(T) + (1 - x) * H_{x2}(T) + \Delta H^{mix}(T, x)$
 - For an ideal mixture $\Delta H^{mix}(T, x) = 0$
- Vapor Mixtures
 - $H_y(T, y) = y * H_{y1}(T) + (1 - y) * H_{y2}(T)$
 - For a mixture of vapors $\Delta H^{mix}(T, x) = 0$

Enthalpy of Mixtures, example

- $$H_x(t,x) = x * 33 * (T - 80.1) + (1 - x) * 40 * (T - 80.1)$$
$$= [33x + 40(1 - x)] * (T - 80.1)$$
$$= (40 - 7x) * (T - 80.1)$$
- $$H_y(T,y) = y * [7360 + 23(T - 80.1)] + (1 - y) * [8174 + 33(T - 80.1)]$$
$$= 8174 - 814y + (33 - 10y) * (T - 80.1)$$

