CE407 SEPARATIONS

Lecture 08

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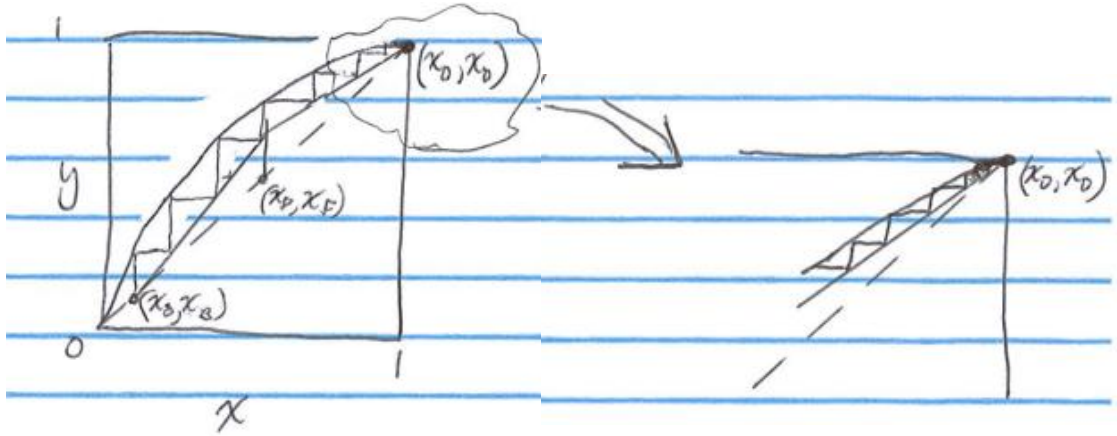
Continuous Distillation with Reflux – Nearly Pure Products

McSH pp 692-694

- What if the purity required is $\mathbf{x_D}$ = 0.9999?



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

What to do for Very High Purity cases?

- In a region a short distance from $\mathbf{x_D}$ = 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 $\mathbf{x_D}$ values extremely close to 1
- We will split the column into two sections with a cutoff value of $\mathbf{x}$, $\mathbf{x_{cutoff}}$
- $\mathbf{x_{cutoff}}$ 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 $\mathbf{x_{cutoff}}$ and $\mathbf{x_D}$ 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
  - $\mathbf{y}^* = \mathbf{y}^*(\mathbf{x}_{\mathbf{cutoff}})$
- In other words , use VLE data or relationship to calculate what value of **y** is in equilibrium with $\mathbf{x}_{\mathbf{cutoff}}$
  - Note that in Excel one can use Goalseek to find the temperature leading to $\mathbf{x} = \mathbf{x}_{\mathbf{cutoff}}$ and then read off $\mathbf{y}^* = \mathbf{y}^*(\mathbf{x}_{\mathbf{cutoff}})$
- Solve for $\mathbf{y} = m\mathbf{x} + b$ that satisfies both (1, 1) and $(\mathbf{x}_{\mathbf{cutoff}}, \mathbf{y}^*(\mathbf{x}_{\mathbf{cutoff}}))$

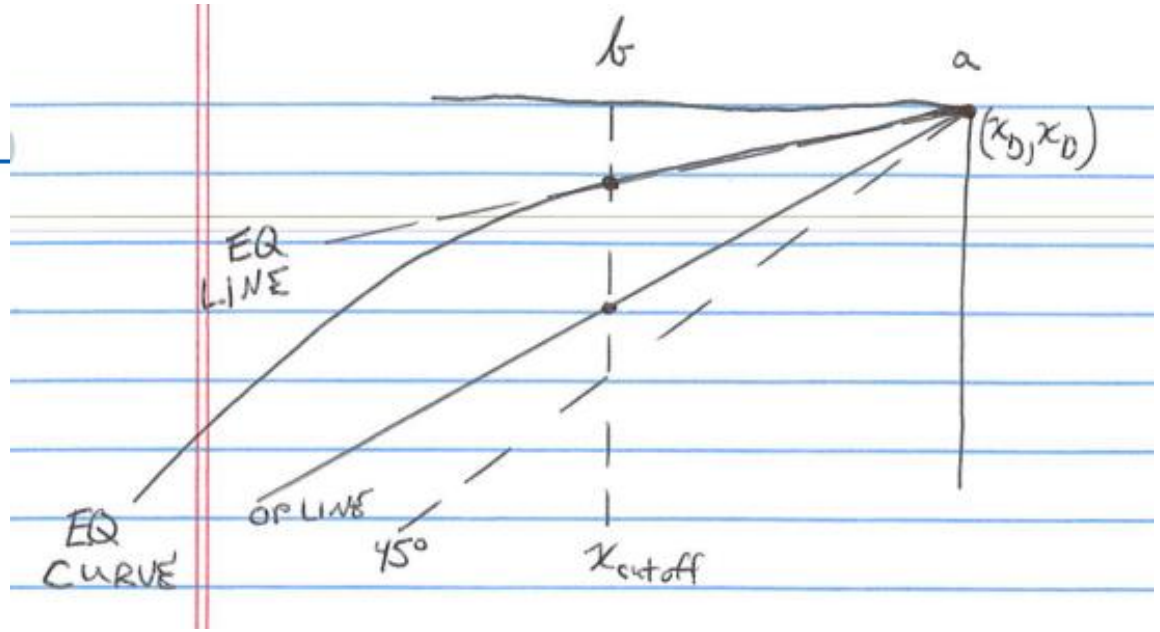
Operating Line

- 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

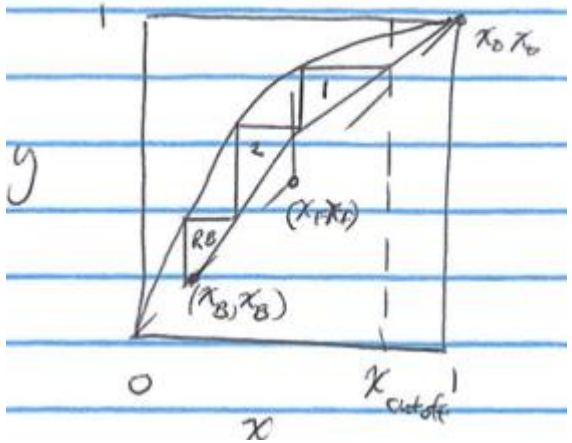
High Purity – Kremser Section



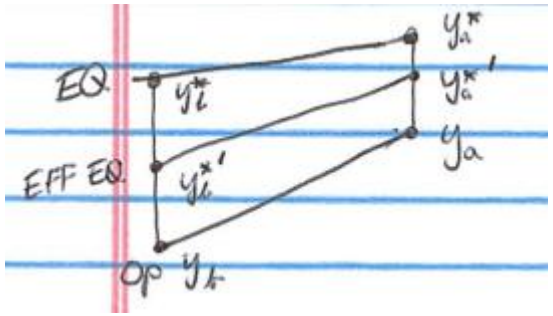
- Kremser Equation $N = \frac{ln[(y_b - y_b^*)/(y_a - y_a^*)]}{ln[(y_b - y_a)/(y_b^* - y_a^*)]}$
- a is at **x = x$_D$**
  - **x$_a$ = x$_D$**
  - **y$_a$ = x$_D$**
  - $y_a^* = y^*(x_D)$ is calculated from the the EQ "Line" **y** = m * **x$_D$** + b
    - Note that the "b" has nothing to do with position 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 $N_{graphical}$
  - In the graph at the right, $N_{graphical}$ = 2 + Reboiler
- $N = N_{Kremser} + N_{graphical}$
- As always, round up for partial stages



High Purity with Non-ideal Stages



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

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

- We want to develop expressions for

$$H_x(T, x) \quad \text{and} \quad H_y(T,y)$$

Liquid Enthalpy Vapor Enthalpy

- 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

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

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

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 $\frac{energy}{mol\,°C}$ eg $\frac{cal}{mol\,°C}$
  - $\Delta H_1^{vap}(T_{nb1})$ is the heat of vaporization of pure component 1 at its normal boiling temperature
  - Because we have chosen a reference of $H_{xi}(T_{nb1}) = 0$

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

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

$$C_{p2}^{V} * (T - T_{nb2}) = C_{p2}^{V} * (T - T_{nb1} + T_{nb1} - T_{nb2})$$
$$= C_{p2}^{V} * (T_{nb1} - T_{nb2}) + C_{p2}^{V} * (T - T_{nb1})$$

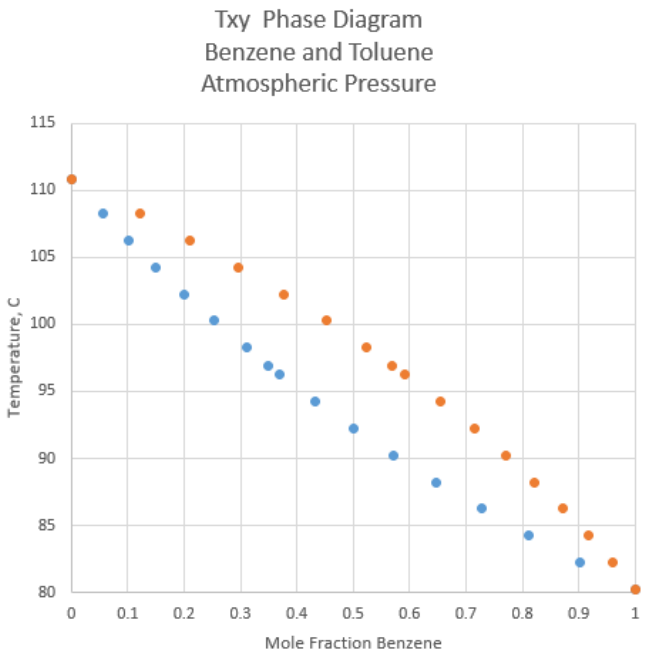
    - This allows all four terms (H_{x1}, H_{x2}, H_{y1}, H_{y2}) to be expressed in terms of $(T - T_{nb1})$
  - Because we have chosen a reference of $H_{xi}(T_{nb1}) = 0$

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

Example

- Benzene (1) and Toluene (2)

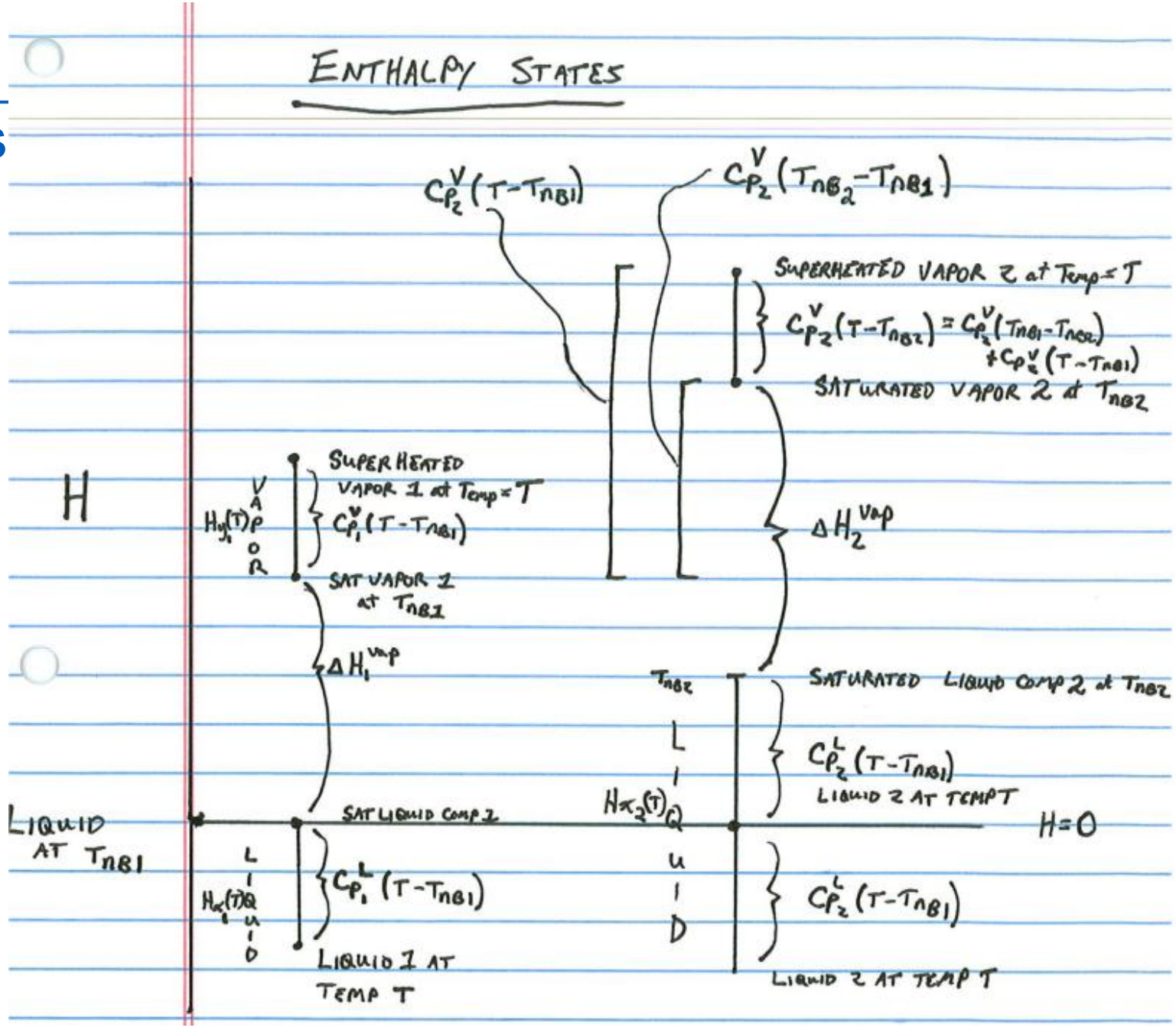
Component	C_{pi}^{L} cal/molC	C_{pi}^{V} cal/molC	ΔH_i^{vap} cal/mol	T_{nbi} C
1	33	23	7360	80.1
2	40	33'	7960	110.6



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

  $= 8174 + 33' * (T - 80.1)$

Enthalpy States



Enthalpy of Mixtures

- Liquid Mixtures
  - $\boldsymbol{H_x(T,x) = x * H_{x1}(T) + (1 - x) * H_{x2}(T) + \Delta H^{mix}(T,x)}$
  - For an ideal mixture $\boldsymbol{\Delta H^{mix}(T,x) = 0}$

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

Enthalpy of Mixtures, example

- $H_x(T,x) = x * 33 * (T - 80.1) + (1 - x) * 40 * (T – 80.1)$

  $= [33x + 40(1 - x)] * (T – 80.1)$

  $= (40 – 7x) * (T – 80.1)$

- $H_y(T,y) = y * [7360 + 23(T – 80.1)] + (1 – y) * [8174 +33(T – 80.1)]$

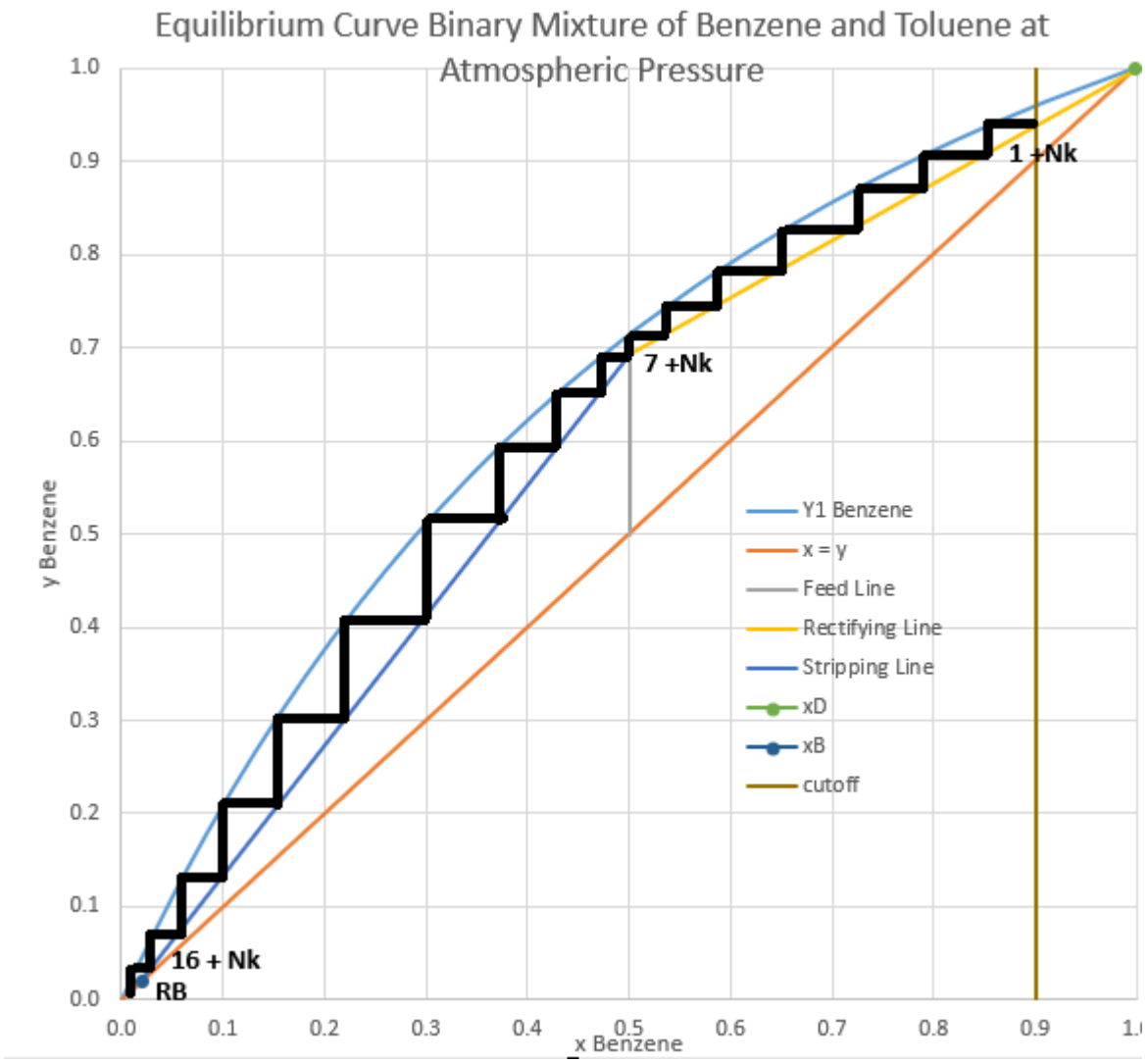
  $= 8174 – 814y + (33 – 10y) * (T – 80.1)$

High Purity, example

- A 100 mole/min feed stream comprising 50 mole percent benzene and 50 mole percent toluene is separated by continuous distillation at atmospheric pressure in a column fitted with a total condenser.
- Process specifications require a mole fraction of 0.999 benzene in the distillate and 0.02 in the bottoms.
- The feed enters as a saturated liquid.
- The reflux ratio $R_D = 1.6$
- Use the analytical procedure (Kremser equation) for $x > 0.9$ and the graphical (McCabe-Thiele method) for $x < 0.9$. Note that one point on the equilibrium curve is **(x,y) = (0.9000000, 0.9587266)**.

High Purity, example

- The only thing new here is that we start our first triangle on the operating line at $x = x_{cutoff}$
- Numbering indicates the stages in addition to the ones calculated using the Kremser equation
- The feed stage is either the 7th or 8th stage below $x = x_{cutoff}$



High Purity, example

- Now we will use the Kremser equation to calculate the number of stages required to get from cutoff value of x = 0.9 to the desired value of x_D = 0.999

$$N = \frac{ln[(y_b - y_b^*)/(y_a - y_a^*)]}{ln[(y_b - y_a)/(y_b^* - y_a^*)]}$$

- $\boldsymbol{y_a}$ = (the point on the R OP line at x = x_D) = x_D **= 0.999**
- $\boldsymbol{y_b}$ = (the point on the R OP line at x = 0.90) = $\frac{R}{R+1} * 0.9 + \frac{x_D}{R+1}$ **= 0.938076923**
- y_b^* = the point on the "equilibrium line" at x_{cutoff} = 0.9. It was given in the problem statement that **(0.9000000, 0.9587266)** is a point on the equilibrium curve, therefore:

  $\boldsymbol{y_b^*}$ **= 0.9587266**

High Purity, example

- In order to determine y_a^* we will need to calculate an equation for the "equilibrium line"
- This line will pass through the point **(0.9000000, 0.9587266)** and the point **(1, 1)** because equilibrium ALWAYS passes through **(1, 1)**
- Solving for the line that passes through these two points leads to:

$$\boldsymbol{y^* = 0.412734375\, x + 0.587265625}$$

- $\boldsymbol{y_a^*}$ **=** (the point on the equilibrium line where x = x_D) = **0.999587266**
- Place these values into the Kremser Equation

$$N = \frac{ln[(y_b - y_b^*)/(y_a - y_a^*)]}{ln[(y_b - y_a)/(y_b^* - y_a^*)]} = 8.9$$

High Purity, example

- The total number of trays required is

$$N_{McT} + N_K + RB = 16 + 8.9 + RB = 25 + RB$$

- Feed enters on tray 7+ N_K = 7 + 9 = 16

High Purity Sensitivity Analysis

- So, we are doing these calculations to a large number of significant figures
- We can't control some of the input variables that tightly
- How much does that change the answer?
- Variation in Feed purity: This table is for R = 1.6 and x_d = 0.999

x_f	N Kremser Stages
0.40	8.9
0.50	8.9
0.60	8.9

- Really not any effect on the Kremser stages
- The McCabe-Thiele graph will give a different number of stages

High Purity Sensitivity Analysis

R	N Kremser Stages
1.5	9.3
1.6	8.9
1.7	8.6

- Variation in Reflux Rate: This table is for $x_f = 0.50$ and $x_d = 0.999$
- You can see a moderate effect on the Kremser stages
- Of course, the McCabe-Thiele graph will give a different number of stages, as well

High Purity Sensitivity Analysis

- Effect of desired purity
- This table is for R = 1.6 and x_f = 0.50

x_d	N Kremser Stages
0.999	8.9
0.9999	14.6
0.99999	20.4

- Large effect on the Kremser stages
- The McCabe-Thiele graph will not give a significantly different number of stages