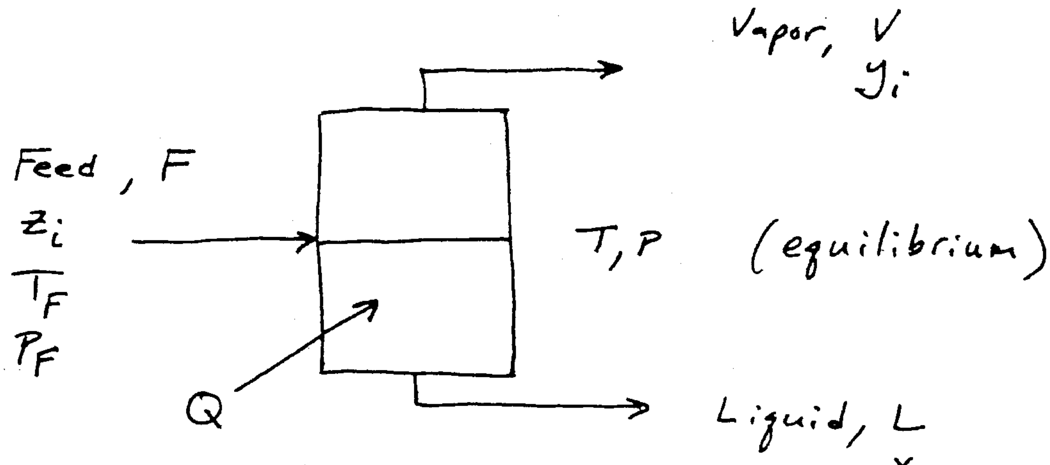
CHAP. 4 NOTES: CHE 305 - SEPARATION PROCESSES

SINGLE EQUILIBRIUM STAGES



VLE

F, V, L molar flow rates (no reaction)

z_i = feed composition

x_i = liquid stream composition

y_i = vapor stream composition

$\left.\begin{array}{l} z_i \\ x_i \\ y_i \end{array}\right\}$ mole fractions

T_F = feed temperature

P_F = feed pressure

T = liquid + vapor stream temperature

P = liquid + vapor stream temperature

Q = heat added (+) to system
(⇒ energy balance)

DEGREES OF FREEDOM

⇒ How well specified is the system?

⇒ What do we need to specify so other variables are set?

⇒ GIBBS PHASE RULE

$$\mathcal{F} = \mathcal{V} - \mathcal{E}$$ (degrees of freedom)

$$\mathcal{V} = C\mathcal{P} + 2$$ (# of intensive variables)

$$\mathcal{E} = \mathcal{P} + C(\mathcal{P}-1)$$ (# of equations)

<u>ASIDE:</u> INTENSIVE VARIABLES

→ DO NOT DEPEND ON SYSTEM SIZE

e.g. T, P, x_i, y_i, c_i

$$\boxed{\mathcal{F} = C - \mathcal{P} + 2}$$

$C \equiv$ # of compinents

$\mathcal{P} \equiv$ # of phases

EXAMPLE:

BINARY VLE

$C = ?$

$P = ?$

$F = ?$

What are the equations?

$y_1 + y_2 = 1$

$x_1 + x_2 = 1$

$K_i = \dfrac{y_i}{x_i}$ } one equation for each component

NOTICE: if given the TXY diagram can calculate K_i @ T (works for ideal or non-ideal since activity coefficient buried in K_i)

Add flow into & out of system:

$$F z_i = V y_i + L x_i$$ one for each component

$$F = V + L \quad \text{(overall)}$$

$$F h_F + Q = V h_V + L h_L$$

NOTE: Only C of the material balances are independent.

RELATIVE VOLATILITY:

$$\alpha_{A,B} = \frac{y_A / x_A}{y_B / x_B} = \frac{y_A / x_A}{(1-y_A)/(1-x_A)}$$

$\alpha_{A,B} > 1.2$ for distillation to be economical

(RULE OF THUMB)

BEWARE:

$$\alpha_{A,B} = f(T, P)$$

(not explicitly) SEE TABLES 4.1, 4.2

EXAMPLE:

from QUIZ

@ 80°C

$x_1 = 0.02$ [redacted]

$y_1 = 0.54$

@ 72°C

$x_1 = 0.72$ [redacted]

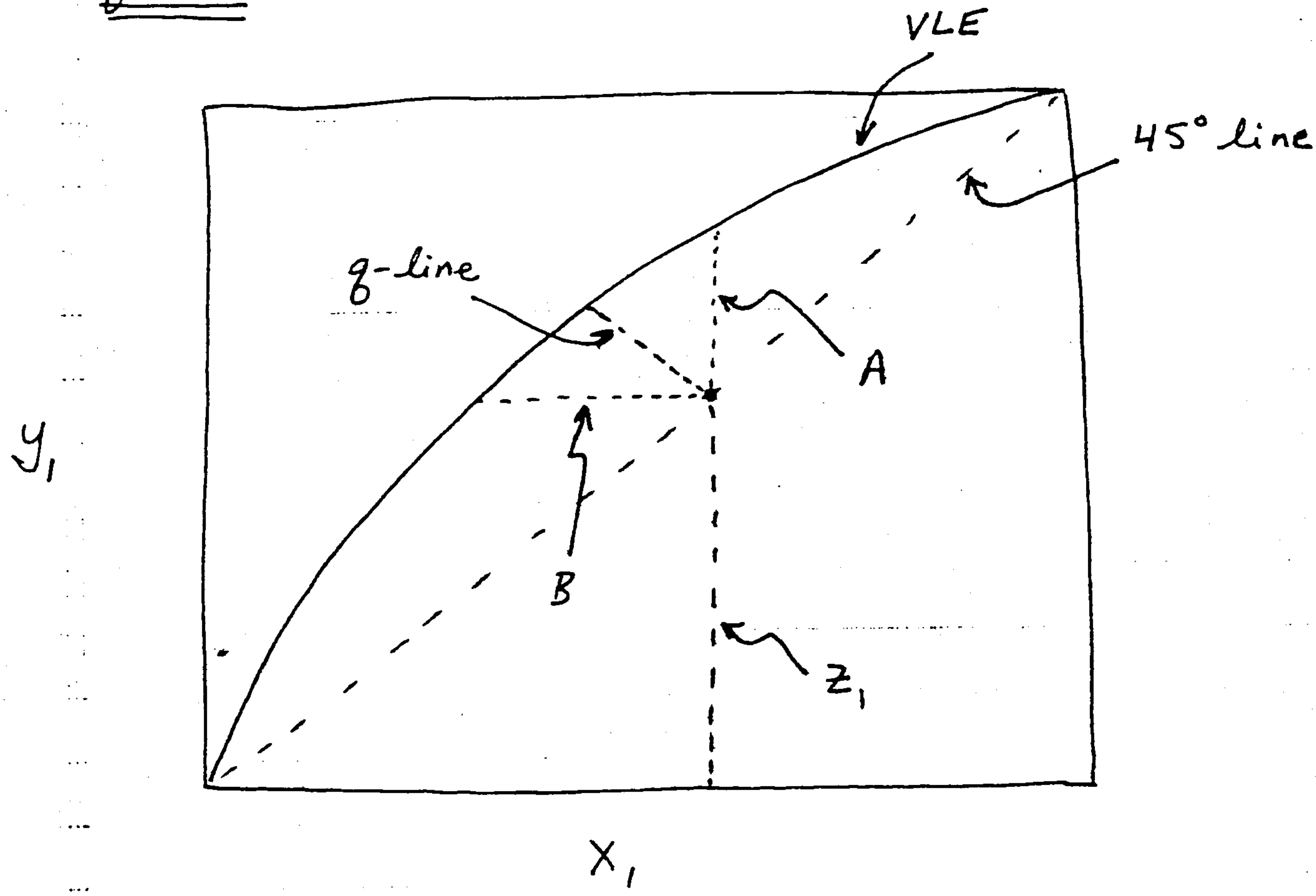
$y_1 = 0.72$

WHY? AZEOTROPE

NOW, WE'VE USED Txy + Pxy DIAGRAMS TO UNDERSTAND WHAT IS OCCURING. WE ALSO MADE XY DIAGRAMS. THESE ARE MOST COMMONLY USED FOR DESIGN.

HOW TO GET x_i + y_i from XY Diagrams GIVEN FEED COMPOSITION?

<u>q-line</u>:



A ≡ q-line w/ operation @ Bubble T

B ≡ q-line w/ operation @ DEW T

⇒ AGAIN, HAVE METHOD TO SEE IF YOUR q-line makes <u>SENSE</u>.

HOW TO GET THE q-LINE:

① Component mole balance, component 1

$$F z_1 = V y_1 + L x_1$$

② Total mole balance

$$F = V + L$$

METHOD:

Eliminate L

Solve for y_1

$$L = F - V$$

$$F z_1 = V y_1 + (F - V) x_1$$

$$V y_1 = F z_1 - (F - V) x_1$$

$$y_1 = \frac{1}{V} \left\{ x_1 (V - F) + z_1 F \right\}$$

$$y_1 = x_1 \left(\frac{V - F}{V} \right) + z_1 \frac{F}{V}$$

<u>INTRODUCE NEW TERM:</u> $\psi = \frac{V}{F}$

$\psi =$ vaporization of feed

e.g. 60% vaporization

$$0.6 = \frac{V}{F} \Rightarrow V = 0.6F$$

$\Rightarrow$ Need $\frac{V}{F}$ in equation

$$y_1 = x_1 \left\{ \frac{(V - F)\frac{1}{F}}{V\frac{1}{F}} \right\} + z_1 \left(\frac{1}{\left(\frac{V}{F}\right)} \right)$$

$$y_1 = x_1 \left\{ \frac{\frac{V}{F} - 1}{\frac{V}{F}} \right\} + z_1 \left(\frac{1}{\left(\frac{V}{F}\right)} \right)$$

$$\boxed{y_1 = x_1 \left(\frac{\psi - 1}{\psi} \right) + z_1 \left(\frac{1}{\psi} \right)} \quad \text{q-line}$$

Slope of q-line: $\frac{\psi - 1}{\psi}$

$\Rightarrow$ Know z_i, know $V, F \Rightarrow$ Can get q-line

ANOTHER PERSPECTIVE ON RELATIVE VOLATILITY

If Raoult's Law Applies...
(ideal gas / ideal liquid)

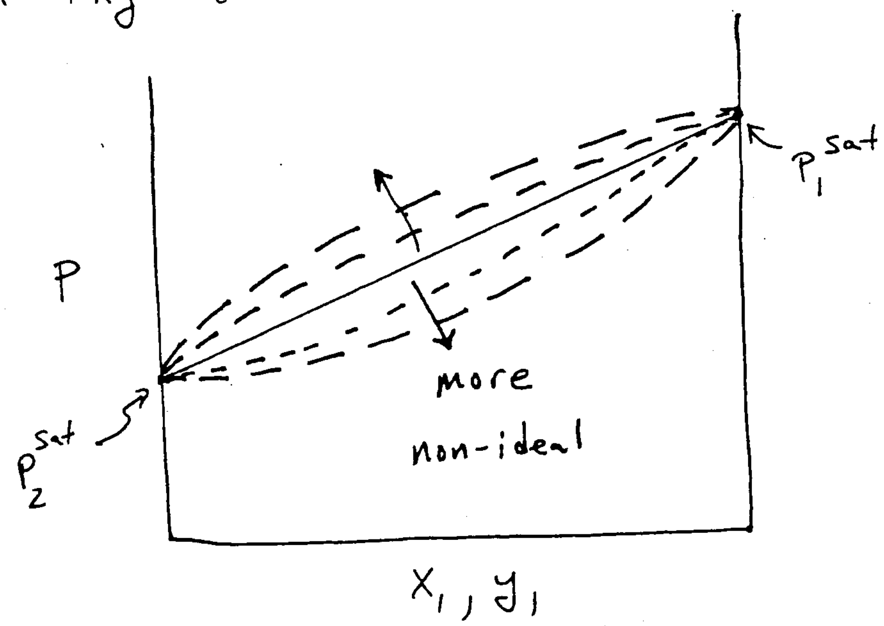
$$P = x_A P_A^{sat} + x_B P_B^{sat}$$

$$P = x_A P_A^{sat} + (1 - x_A) P_B^{sat}$$

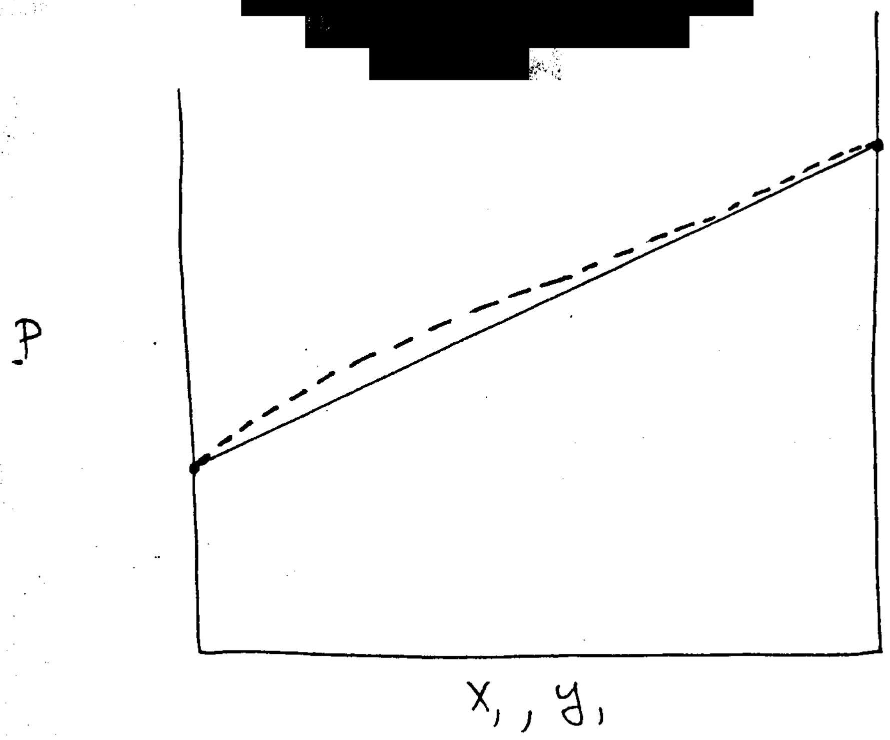
$$P = P_B^{sat} + x \left(P_A^{sat} - P_B^{sat} \right)$$

$P_i^{sat} = f(T)$ only $\Rightarrow$ constant if T set.

Recall Pxy (Raoult's Law)



linear



Small changes from Ideal

y_A can be written in terms of x_A + α_{AB}

Recall $$\alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B}$$

Solve for y_A (eliminate y_B, x_B)

$$\alpha_{AB} = \frac{y_A \;(1 - x_A)}{x_A \;(1 - y_A)}$$

$$\alpha_{AB}\, x_A\, (1 - y_A) = y_A\, (1 - x_A)$$

$$\alpha_{AB}\, x_A - \alpha_{AB}\, x_A\, y_A = y_A\, (1 - x_A)$$

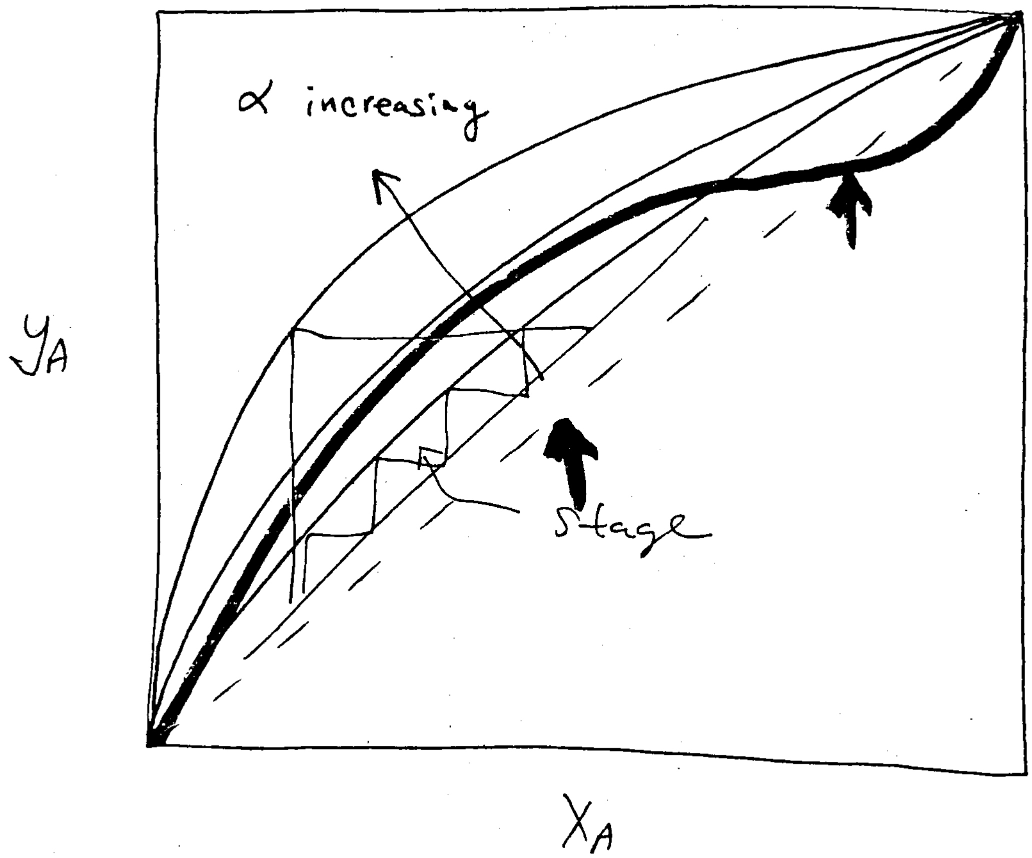
$$\alpha_{AB}\, x_A = y_A\, (1 - x_A + \alpha_{AB}\, x_A)$$

$$\Rightarrow \boxed{y_A = \frac{\alpha_{AB}\, x_A}{1 + x_A\,(\alpha_{AB} - 1)}}$$

Can use this to get xy diagram for systems w/ ~ stable α_{AB}.

Particularly true for idealsystem...

$$\alpha_{AB} = \frac{K_A}{K_B} = \frac{\left(\frac{P_A^{sat}}{P}\right)}{\left(\frac{P_B^{sat}}{P}\right)} = \frac{P_A^{sat}}{P_B^{sat}}$$



Constant α_{AB}

Where is $\alpha = 1$ (No separation)?

MORE ON AZEOTROPES:

CONDITIONS

1) $y_i = x_i$

2) $K_i = 1$

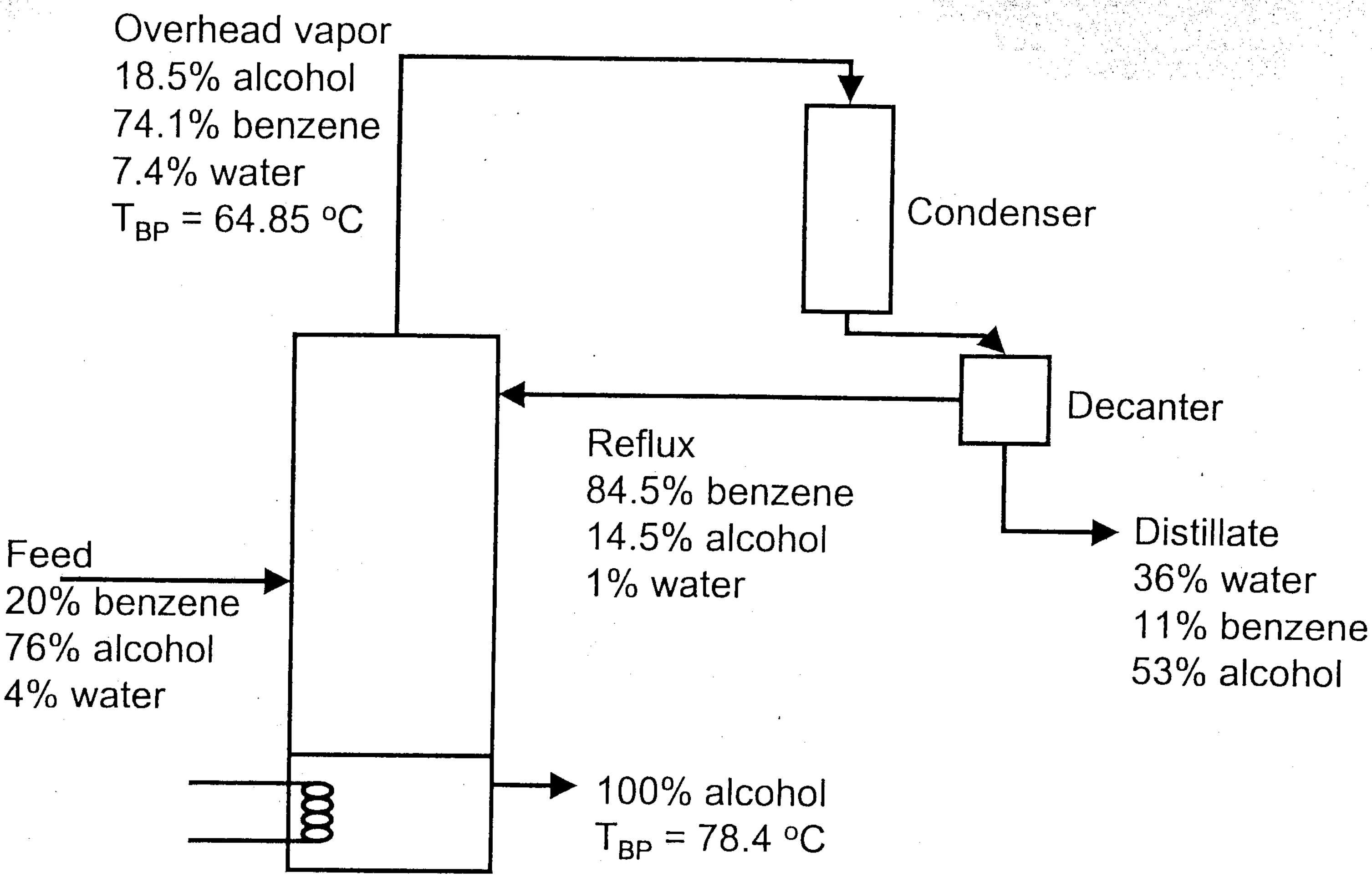
Azeotrope $\Rightarrow$ departure from ideality

How can I make a system more ideal?

LOWER PRESSURE

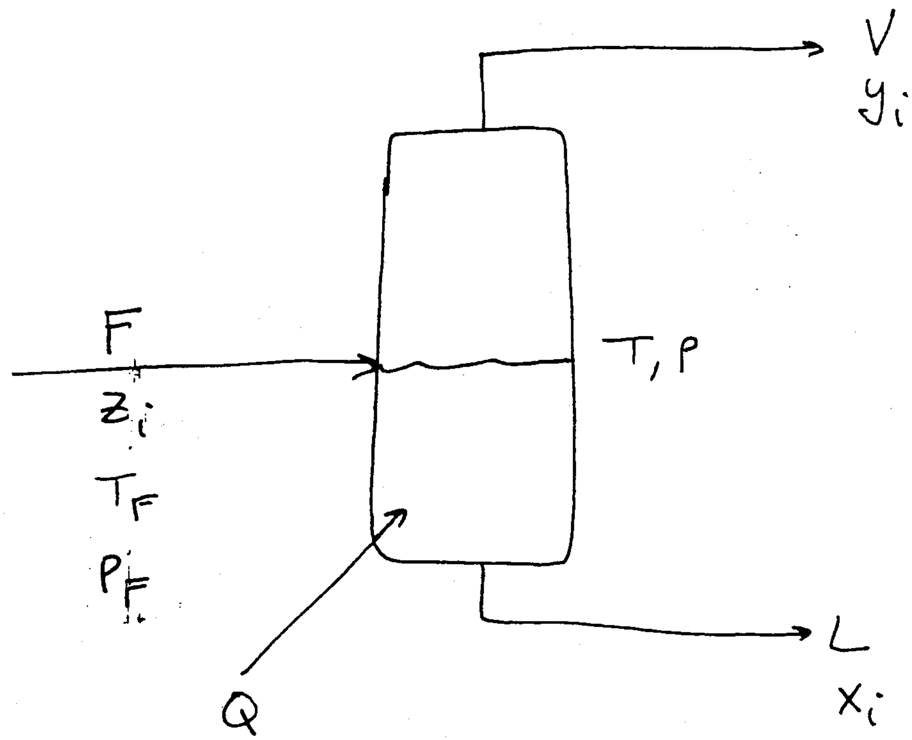
$\Rightarrow$ VACUUM DISTILLATION

See Chem Cad



Keyes Process for Absolute Alcohol (Figure 4.9 Seader and Henley)

MORE ON FLASH CALCULATIONS



NOTES:

- z_i

  OVERALL COMPOSITION

  ⇒ COMPOSITION IF ONE PHASE

- HOW MANY UNKNOWNS ?

  ⇒ GIBBS PHASE RULE

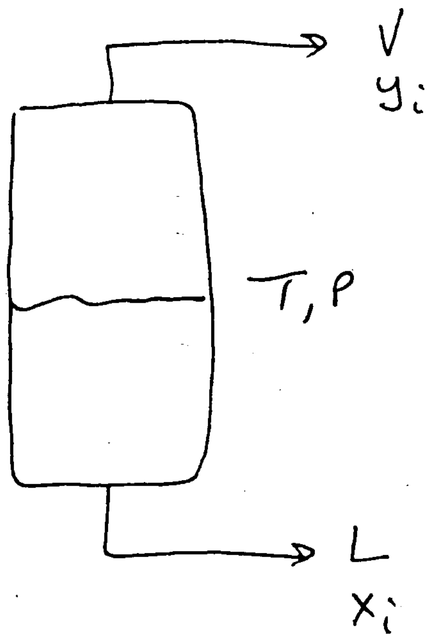
[redacted]

RECALL:

GIBBS PHASE RULE

$$F = C - P + 2$$

GIVES # OF INTENSIVE VARIABLE DEGREES OF FREEDOM FOR



ADD STREAMS FLOWING IN &

Add New Variables

F, T_F, P_F, z_i

NICE THING IS THAT WE USUALLY KNOW WHAT THESE ARE.

$\Rightarrow$ DEGREES OF FREEDOM FOR BINARY 2-PHASE FLASH

$$C + 5 = 7$$

WE KNOW 5

$$F,\ T_F,\ P_F,\ z_1,\ z_2$$

NEED TO SET $\underline{\underline{2}}$ MORE.

KNOW	SITUATION
$T_V,\ P_V$	Isothermal Flash
$\psi = 0,\ P_L$	BUBBLE POINT T
$\psi = 1,\ P_V$	DEW POINT T
$\psi = 0,\ T_L$	BUBBLE POINT P
$\psi = 1,\ T_V$	DEW POINT P

MISTAKE IN BOOK.

$Q = 0,\ P_V$ ADIABATIC FLASH

$Q,\ P_V$ NON ADIABATIC FLASH

$\Psi,\ P_V$ % Vaporization Flash

(p. 178 in Chap. 4, Seader & Henley)

ISOTHERMAL FLASH:

KNOW FEED CONDITIONS $\Rightarrow$

SPECIFY $T_V,\ P_V$

EQUATIONS:

1) MECHANICAL EQUILIBRIUM

$$P_V = P_L \qquad (1)$$

2) THERMAL EQUILIBRIUM

$$T_V = T_L \qquad (1)$$

3) PHASE EQUILIBRIUM

$$K_i = \frac{y_i}{x_i} \qquad C$$

4) COMPONENT MOLE BALANCES

$$F z_i = V y_i + L x_i \qquad C$$

5) TOTAL MOLE BALANCE

$$F = V + L \qquad 1$$

6) SUMMATIONS

$$\sum_i x_i = 1$$

$$\sum_i y_i = 1 \qquad 2$$

(Note: only C mole balances independent)

7) ENERGY BALANCE

$$F h_F + Q = V h_V + L h_L \qquad 1$$

HOW TO SOLVE?

RACHFORD – RICE (TABLE 4.4)

⇒ ASSUMPTION:

K-values constant

⇒ Ideal or close to ideal.

w/ Specified

$$F, T_F, P_F, z_1, z_2, T_V, P_V$$

STEPS:

1) Thermal Equilibrium

$$T_V = T_L$$

2) Mechanical Equilibrium

$$P_V = P_L$$

3) Solve:

$$f(\Psi) = \sum_{i=1}^{C} \frac{z_i(1-K_i)}{1+\Psi(K_i-1)} = 0$$

WHERE DOES THIS COME FROM?

A CONVOLUTED PATH TOWARD $f(\Psi)$ ...

$$1 = 1$$

$$X_1 + X_2 = y_1 + y_2$$

$$X_1 - y_1 + X_2 - y_2 = 0$$

$$\frac{Fz_1 (X_1 - y_1)}{Fz_1} + \frac{Fz_2 (x_2 - y_2)}{Fz_2} = 0$$

Expand Denominators + Add Zero ...

$$\frac{Fz_1 (X_1 - y_1)}{Lx_1 + Vy_1 + Vx_1 - Vx_1} + \frac{Fz_2 (x_2 - y_2)}{Lx_2 + Vy_2 + Vx_2 - Vx_2} = 0$$

$$\frac{Fz_1 (X_1 - y_1)}{F(x_1) + Vy_1 - Vx_1} + \frac{Fz_2 (X_2 - y_2)}{Fx_2 + Vy_2 - Vx_2} = 0$$

NEXT WE SEE WHY WE HAD F...

MULTIPLY TOP & BOTTOM BY $\frac{1}{F}$ ...

$$\frac{z_1 (x_1 - y_1)}{x_1 + \frac{V}{F}(y_1 - x_1)} + \frac{z_2 (x_2 - y_2)}{x_2 + \frac{V}{F}(y_2 - x_2)} = 0$$

BUT FINAL EQUATION HAD K_i

SO, MULTIPLY TOP & BOTTOM BY RESPECTIVE $\frac{1}{x_i}$

$$\frac{z_1 \left(1 - \frac{y_1}{x_1}\right)}{1 + \underbrace{\frac{V}{F}}_{\psi}\left(\underbrace{\frac{y_1}{x_1}}_{K_1} - 1\right)} + \frac{z_2 \left(1 - \frac{y_2}{x_2}\right)}{1 + \frac{V}{F}\left(\underbrace{\frac{y_2}{x_2}}_{K_2} - 1\right)} = 0$$

$$\frac{z_1 (1 - K_1)}{1 + \psi (K_1 - 1)} + \frac{z_2 (1 - K_2)}{1 + \psi (K_2 - 1)} = 0$$

$$\boxed{\sum_{i=1}^{c} \frac{z_i (1 - K_i)}{1 + \psi (K_i - 1)} = 0} \leftarrow f(\psi)$$

BACK TO STEP 3

$$f(\Psi) = \sum_{i=1}^{C} \frac{z_i (1 - K_i)}{1 + \Psi (K_i - 1)} = 0$$

REMEMBER, $K_i = f(T_V, P_V)$

Raoult's Law

$$y_i P = x_i P_i^{sat}$$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P}$$

Solve for Ψ.

4) $V = F \Psi$ (Ψ definition)

5) $$x_i = \frac{z_i}{1 + \Psi (K_i - 1)}$$

WHERE DOES THIS COME FROM?

STARTING FROM COMPONENT MOLE BALANCE

$$L x_i + V y_i = F z_i$$

$$\underbrace{L x_i + V x_i} + V y_i - V x_i = F z_i$$

$$\left\{ F x_i + V y_i \frac{x_i}{x_i} - V x_i = F z_i \right\} \frac{1}{F}$$

$$x_i + \frac{V}{F} x_i \left(\frac{y_i}{x_i} - 1 \right) = z_i$$

$$x_i \left(1 + \psi \left(K_i - 1 \right) \right) = z_i$$

$$x_i = \frac{z_i}{1 + \psi (K_i - 1)}$$

6) $y_i = K_i x_i$ (Raoult's Law)

7) $L = F - V$ (Overall Mole Balance)

8) ENERGY BALANCE IF NEEDED.

⇒ KNOW THE STEPS ...
BUT HOW DO WE DO IT???

(Remember, STEP 3 in nonlinear & getting ψ is <u>not</u> trivial)

⇒ WOULD LIKE TO HAVE SOME RATIONAL PROCESS

⇒ ITERATIVE SOLUTION BY NEWTON'S METHOD

RECALL

NEWTON'S METHOD

GIVEN $f(X) = 0$

METHOD LETS US FIND $X = X_R$ BY ITERATION.

ROOT

$$X_{j+1} = X_j - \frac{f(X_j)}{f'(X_j)}$$

New GUESS

GUESS

TEST!

$$\frac{X_{j+1} - X_j}{X_j} < \text{tolerance}$$

NEED TO USE YOUR JUDGEMENT HERE.

BACK TO ISOTHERMAL FLASH...

from Newton's Method, need $f'(x)$

REMEMBER STEP 3

$$\underline{\underline{f(\psi)}} = \sum_{i=1}^{C} \frac{z_i\,(1-K_i)}{1+\psi\,(K_i-1)} = \underline{\underline{0}}$$

HERE IS OUR FUNCTION FOR NEWTON'S METHOD.

$\Rightarrow$ NEED $f'(\psi)$

$\Rightarrow$ Differentiation with respect to $\underline{\underline{\psi}}$

LET'S LOOK AT WHAT'S INSIDE SUMMATION...

$$\frac{z_i\,(1-K_i)}{1+\psi\,(K_i-1)}$$

z_i + K_i constant.

$$f = \sum_{i=1}^{c} z_i (1-K_i) \left[1 + \psi (K_i - 1) \right]^{-1}$$ (rewrite)

$$\frac{df}{d\psi} = \sum_{i=1}^{c} z_i (1-K_i)(-1)\left[1 + \psi (K_i - 1) \right]^{-2} (K_i - 1)$$

$$= \sum_{i=1}^{c} \frac{-z_i (1-K_i)(K_i - 1)}{\left[1 + \psi (K_i - 1) \right]^{2}}$$

$$\boxed{f'(\psi) = \sum_{i=1}^{c} \frac{z_i (1-K_i)^2}{\left[1 + \psi (K_i - 1) \right]^{2}}}$$

Now, let's solve Step 3 . . .

z_i given

$K_i = f(T)$ only.

Next, guess ψ_j $(j=0)$ initial guess

Remember, $0 \le \varphi \le 1$, so have an easy way to choose. (e.g., $\varphi = 0.5$).

1. $\varphi_j = 0.5$

2. Calculate $f(\varphi_j)$ ← No: $\varphi_j = \varphi_{j+1}$

3. Calculate $f'(\varphi_j)$

4. New $\varphi \Rightarrow \varphi_{j+1}$

$$\varphi_{j+1} = \varphi_j - \frac{f(\varphi_j)}{f'(\varphi_j)}$$

5. Test: $\dfrac{\varphi_{j+1} - \varphi_j}{\varphi_j} <$ tolerance

↓ yes

<u>done</u>