

CHAP. 10 INTRODUCTION TO VAPOR/LIQUID
EQUILIBRIUM.

⇒ THERMODYNAMICS OF SEPARATIONS

BEFORE:

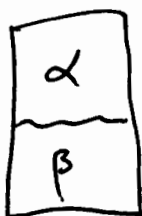


TWO PHASES
 $\alpha + \beta$

COMPOSITION OF $\alpha + \beta$ SAME
(one component)

WHAT ABOUT MULTIPLE COMPONENT SYSTEMS?

NOW:



TWO PHASES
 $\alpha + \beta$

COMPOSITION OF $\alpha + \beta$ DIFFERENT
 $y_{\alpha} \neq x_{\beta}$

NOTE: $T_{\alpha} = T_{\beta}$, $P_{\alpha} = P_{\beta}$

EXPRESSIONS FOR COMPOSITION:

VAPOR PHASE:

- y_i (mole or mass fraction)
- P_i (partial pressure)
- n_i (moles component "i")
- m_i (mass component "i")

M = total mass of vapor phase

n = total moles of vapor phase

$\Rightarrow y_i = \frac{n_i}{n}$

└──────────┘
mole fraction

$y_i = \frac{m_i}{M}$

└──────────┘
mass fraction

} Gas
Phase

Beware: $\frac{n_i}{n} \neq \frac{m_i}{M}$

\Rightarrow Make sure to check if mass or moles.

Nice thing about mass & mole fractions:

$$\sum_i \frac{n_i}{n} = 1 \quad \text{and} \quad 0 \leq \frac{n_i}{n} \leq 1$$

$$\sum_i \frac{M_i}{m} = 1 \quad \text{and} \quad 0 \leq \frac{M_i}{m} \leq 1$$

Finally, Partial Pressure...

$$P_i = y_i P \leftarrow \text{Total Pressure.}$$

↑
mole fraction of component "i"

AND

$$\sum_i P_i = P$$

How about liquid phase?

$$X_i = \frac{n_i}{n}$$

↳
mole fraction

$$X_i = \frac{M_i}{m}$$

↳
mass fraction

BEWARE: $\frac{n_i}{n} \neq \frac{m_i}{m}$

Also: $\sum_i x_i = 1$ and $0 \leq x_i \leq 1$

Finally: Concentration

if mass:

$$C_i = \frac{m_i}{V} [=] \frac{\text{mass}}{\text{volume}} \quad (\text{units of } \rho)$$

if moles:

$$C_i = \frac{n_i}{V} [=] \frac{\text{mol}}{\text{volume}} \quad (\text{units of molar } \rho)$$

In both cases,

$$\sum_i C_i = C_T \quad \swarrow \text{total concentration}$$

AND, $M = \sum_i x_i M_i$ MOLAR MASS OF A SOLUTION

(5)

10.2 THE PHASE RULE. DUHEM'S THEOREM.

⇒ COMPOSITIONS ARE INTENSIVE (y_i, x_i, P_i, c_i)
AND EXTENSIVE (n_i, m_i).

THE INTENSIVE VARIABLES OBEY THE PHASE RULE.

⇒ EXAMPLE:

$$F = 2 - \pi + N$$

if $F=2$ + $T+P$ Specified,
then c_i, x_i, y_i, P_i also set.

10.4 SIMPLE MODELS FOR VLE

WE ALREADY KNOW $y_i \neq x_i$ FOR MIXTURES.
(MOST CASES)

WHEN IS THIS NOT THE CASE?

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HOWEVER,

$$y_i \propto x_i$$

or

$$y_i = K_i x_i$$

Proportionality Constant.

How to GET K_i ?

TWO SIMPLE MODELS.

RAULT'S LAW:

$$y_i P = x_i P_i^{sat} \quad (i = 1, 2, \dots, N)$$

$$\Rightarrow K_i = \frac{P_i^{sat}}{P}$$

ASSUMPTIONS: 1) IDEAL GAS
2) IDEAL LIQUID

} \Rightarrow NO
INTERACTIONS

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⇒ ASK YOURSELF 2 QUESTIONS.

1) IS THE GAS PHASE IDEAL?

→ LOW to MODERATE PRESSURE

→ LARGE VOLUME

2) IS THE LIQUID PHASE IDEAL?

→ ANY SPECIFIC INTERACTIONS?

a) H-Bonding

b) Pi-Pi Stacking

c) Electrostatic

d) Polar molecules

e) BIG DIFFERENCES BETWEEN MOLECULES
IN SOLUTION.

GOOD EXAMPLE IDEAL SOLUTION:

ALKANES, MIXTURES OF AROMATICS

WHEN NON-IDEAL?

WATER + OTHER H-BONDING MOLECULES

BACK TO RAOULT'S LAW:

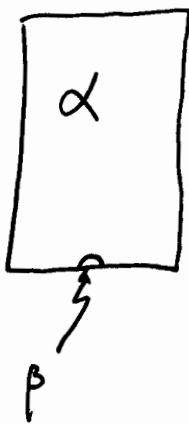
$$y_i P = x_i P_i^{\text{sat}}$$

mole fraction vapor \nearrow y_i \nearrow Total Pressure \nearrow P = x_i \nearrow mole fraction liquid \nearrow x_i \nearrow Vapor Pressure Pure Component "i" \nearrow P_i^{sat}
 $= f(T)$ only
 (Antoine Egn.)

\Rightarrow LOTS OF LIMITATIONS, BUT NOT BAD FOR MOST THINGS AS $x_i \rightarrow 1$.

Dewpoint + Bubblepoint Calculations w/ Raoult's Law:

FIRST, WHAT IS A DEWPOINT?



$\alpha \equiv$ Vapor Phase

$\beta \equiv$ Liquid Phase

Dewpoint: Last drop of liquid vaporized

or

First drop of liquid condensed.

Practically: $V = F$

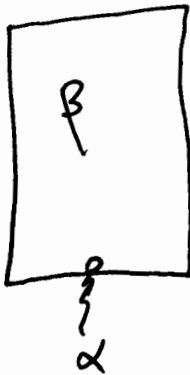
$$L = 0$$

where $V =$ Volume for Vapor Phase

$L =$ Volume of Liquid Phase

$F =$ Total Volume.

NEXT, WHAT IS A BUBBLEPOINT?



$\alpha \equiv$ Vapor Phase

$\beta \equiv$ Liquid Phase

Bubblepoint: First bubble of vapor formed

or
Last bubble of vapor condensed.

SO, WHAT ARE DEW + BUBBLE POINT CALCULATIONS?

FROM PHASE RULE:

$$F = 2 - \pi + N$$

IF 2 COMPONENT + 1 PHASE

(RECALL @ DEW POINT $V = F + L = 0$)

$$\Rightarrow F = 2 - 1 + 2 = 3$$

\Rightarrow SPECIFY 3 PARAMETERS + ALL OTHER INTENSIVE VARIABLES ARE FIXED.

WHAT VARIABLES?

$X_i, y_i, P, T.$ where $i = 1 + 2$

$\Rightarrow X_1, X_2, y_1, y_2, P, T \Rightarrow$ 6 variables

4 CASES:

① BUBBLE P:

\Rightarrow WANT COMPOSITION OF FIRST BUBBLE + WANT P.

\Rightarrow HAVE SPECIFIED $X_1, X_2, T.$

② DEW P

WANT: x_1, x_2, P

HAVE: y_1, y_2, T

③ BUBBLE T

WANT: y_1, y_2, T

HAVE: x_1, x_2, P

④ DEW T

WANT: x_1, x_2, T

HAVE: y_1, y_2, P

RECALL: $y_i P = x_i P_i^{\text{sat}}$ (RAOULT'S LAW)

WRITE FOR EACH COMPONENT:

$$y_1 P = x_1 P_1^{\text{sat}}$$

$$+ y_2 P = x_2 P_2^{\text{sat}}$$

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

$$\Rightarrow P = X_1 P_1^{\text{sat}} + X_2 P_2^{\text{sat}}$$

BUT $\sum_i X_i = 1 \Rightarrow X_1 + X_2 = 1$

Substitute for X_2

$$P = X_1 P_1^{\text{sat}} + (1 - X_1) P_2^{\text{sat}}$$

$$P = P_2^{\text{sat}} + X_1 (P_1^{\text{sat}} - P_2^{\text{sat}})$$

OR

$$P = \frac{1}{\sum_i \left(\frac{y_i}{P_i^{\text{sat}}} \right)}$$

NOTE:

P_i^{sat} BY

ANTOINE
EQUATION

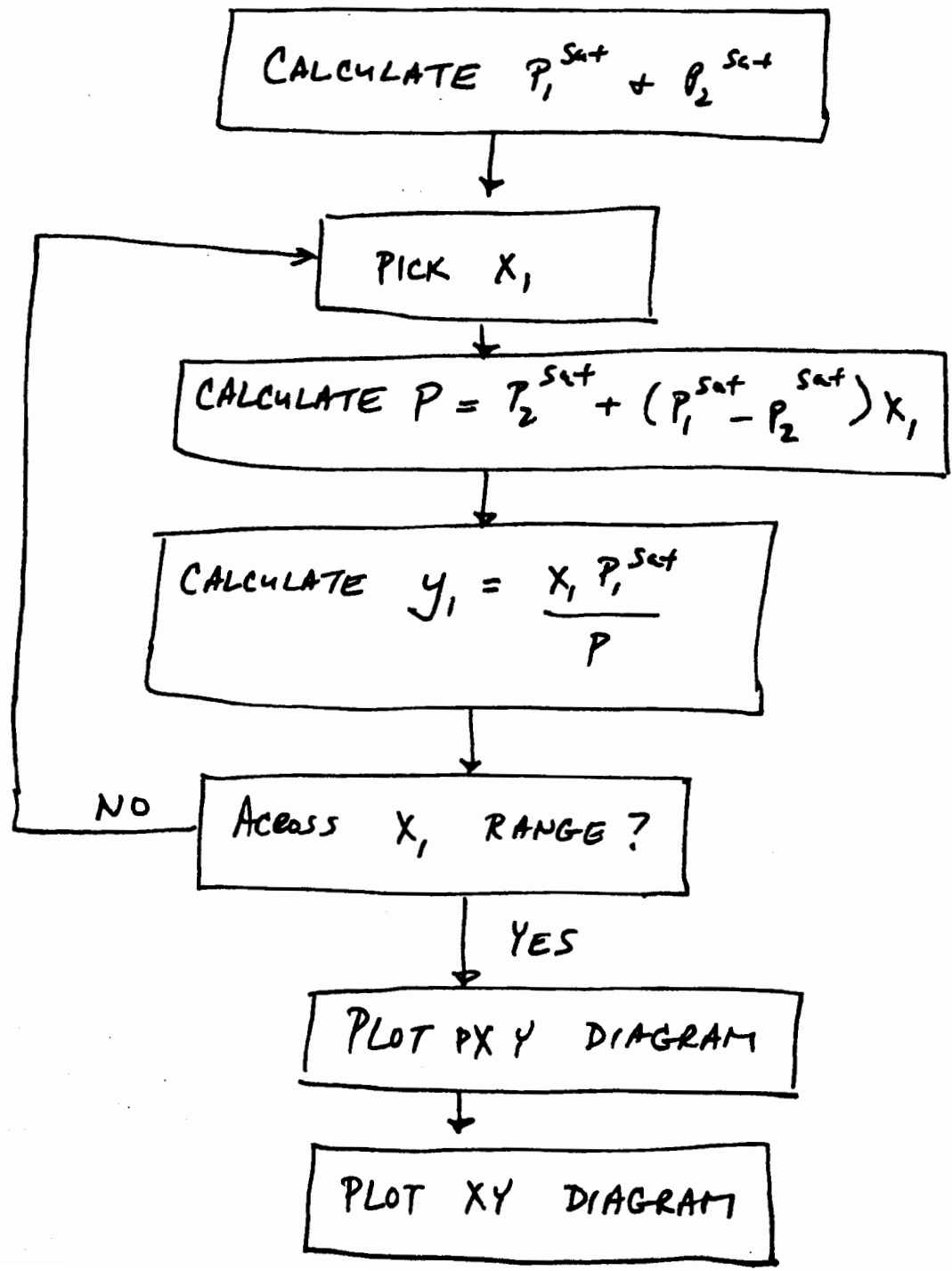
\Rightarrow Phase Diagrams for IDEAL GAS/
IDEAL LIQUID.

(SEE ATTACHED FLOW CHARTS.)

(IN CLASS EXERCISE)

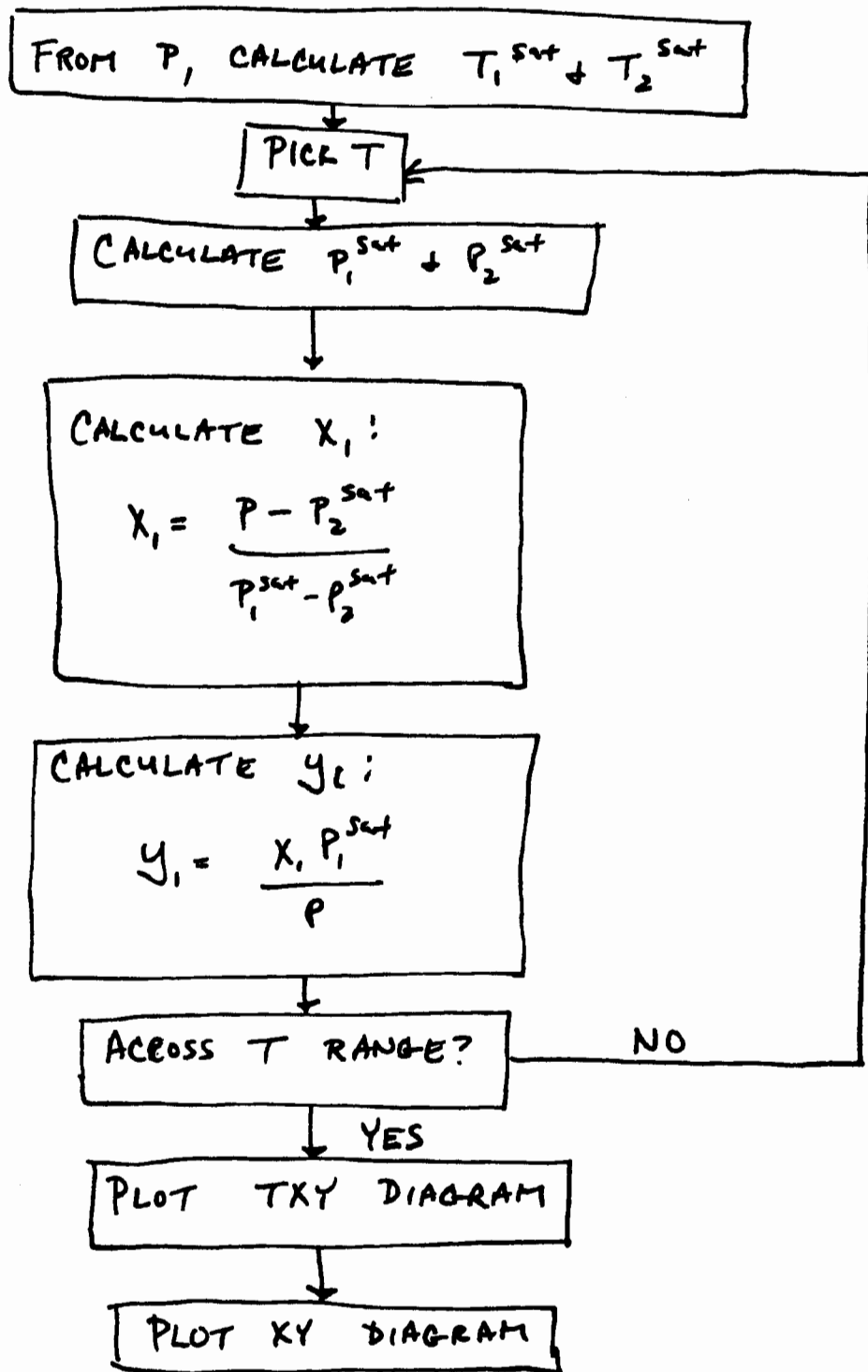
PXY (IDEAL GAS / IDEAL LIQUID)

- RAOULT'S LAW APPLIES
- ANTOINE EQN. FOR P_i^{sat}
- CONSTANT T



TXY (IDEAL GAS/IDEAL LIQUID)

- RAULT'S LAW APPLIES
- ANTOINE EQUATION FOR P_i^{sat}
- CONSTANT P



WHAT TO DO IF $T > T_c$?
(NO P_i^{sat})

⇒ HENRY'S LAW :

$$y_i P = x_i H_i$$

↑
Henry's Law Constant

Values of H_i in Table 10.1 (p. 357)

EXAMPLE 10.2

ASSUMING THAT CARBONATED WATER CONTAINS ONLY $CO_2(l)$ AND $H_2O(l)$, DETERMINE THE COMPOSITIONS OF THE VAPOR AND LIQUID PHASES IN A SEALED CAN OF SODA AND THE PRESSURE EXERTED ON THE CAN AT $10^\circ C$. HENRY'S LAW CONSTANT FOR CO_2 IN WATER AT $10^\circ C$ IS ABOUT 990 bar.

GIVEN: $X_{CO_2} = 0.01$.

PHASE RULE: $F = 2 - 2 + 2 = 2$

GIVEN: $T = 283 K$
 $X_{CO_2} = 0.01$

⇒ All other intensive variables set.

$$\underline{\text{CO}_2}: \quad y_{\text{CO}_2} P = X_{\text{CO}_2} \mathcal{H}_{\text{CO}_2}$$

$$\underline{\text{H}_2\text{O}}: \quad y_{\text{H}_2\text{O}} P = X_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\text{sat}}$$

SUM

$$\underbrace{P(y_{\text{CO}_2} + y_{\text{H}_2\text{O}})}_{=1} = X_{\text{CO}_2} \mathcal{H}_{\text{CO}_2} + X_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$X_{\text{CO}_2} = 0.01 \quad \Rightarrow \quad X_{\text{H}_2\text{O}} = 0.99$$

$$\mathcal{H}_{\text{CO}_2} = 990 \text{ bar (given)}$$

$$P_{\text{H}_2\text{O}}^{\text{sat}} \text{ (steam table @ } 10^\circ\text{C)} = 1.227 \text{ kPa} \\ = 0.01227 \text{ bar}$$

⇒ Plug + Chug

$$P = (0.01)(990 \text{ bar}) + (0.99)(0.01227 \text{ bar})$$

$$\boxed{P = 9.912 \text{ bar}}$$

SO,

$$y_{\text{CO}_2} = \frac{X_{\text{CO}_2} P_{\text{CO}_2}}{P}$$

$$= \frac{(0.01)(990 \text{ bar})}{9.912 \text{ bar}}$$

$$y_{\text{CO}_2} = 0.9988$$

$$\Rightarrow y_{\text{H}_2\text{O}} = 1 - 0.9988 = 0.0012 = y_{\text{H}_2\text{O}}$$

$$\text{Check: } y_{\text{H}_2\text{O}} = \frac{(0.99)(0.01227)}{9.912} = 0.0012 \checkmark$$

Next time: Modified RAULT'S LAW

(LIQUID GOES NON IDEAL)

10.5 VLE BY MODIFIED RAULT'S LAW.

⇒ LOW TO MODERATE PRESSURE

⇒ NON-IDEAL LIQUID.

$$y_i P = x_i \gamma_i P_i^{\text{sat}}$$

ACTIVITY COEFFICIENT

$$K_i = \frac{\gamma_i P_i^{\text{sat}}}{P}$$

$$P = \sum_i x_i \gamma_i P_i^{\text{sat}}$$

or

$$P = \frac{1}{\sum_i \left(\frac{y_i}{\gamma_i P_i^{\text{sat}}} \right)}$$

ACTIVITY COEFFICIENT, γ_i :

FROM ACTIVITY COEFFICIENT MODEL

- SIMPLE: (Polynomial)
- MARGULES - 2 SUFFIX
- VAN LAAR
- MARGULES - 3 SUFFIX

LOCAL COMPOSITION:

- WILSON
- NRTL

GROUP CONTRIBUTION:

- UNIFAC
- UNIQUAC

⇒ DETAILS IN CHAP. 12



EXAMPLE 10.3

FOR THE SYSTEM METHANOL (1) / METHYL ACETATE (2), THE FOLLOWING EQUATIONS PROVIDE A REASONABLE CORRELATION FOR THE ACTIVITY COEFFICIENTS:

$$\ln \gamma_1 = A X_2^2$$

$$\text{where } A = 2.771 - 0.00523 T$$

$$\ln \gamma_2 = A X_1^2$$

AND,

$$\ln P_1^{\text{sat}} = 16.59158 - \frac{3,643.31}{T - 33.424}$$

$$\ln P_2^{\text{sat}} = 14.25326 - \frac{2,665.54}{T - 53.424}$$

WHERE T IS IN K AND P IS IN kPa.

(a) Calculate P and y_i for $T = 318.15 \text{ K}$ + $X_1 = 0.25$

(b) Calculate P and X_i for $T = 318.15 \text{ K}$ + $y_1 = 0.60$

(c) Calculate T and y_i for $P = 101.33 \text{ kPa}$ + $X_1 = 0.85$

(d) Calculate T and X_i for $P = 101.33 \text{ kPa}$ + $y_1 = 0.40$

(a) Calculate $P + y_i$ w/ $T = 318.15K + X_1 = 0.25$
 $\Rightarrow X_2 = 0.75$

$$A = 2.771 - 0.00523(318.15) = 1.1071$$

$$\ln \gamma_1 = 1.1071 X_2^2 \Rightarrow \gamma_1 = 1.8640$$

$$\ln \gamma_2 = 1.1071 X_1^2 \Rightarrow \gamma_2 = 1.0716$$

$$P_1^{sat} = \exp \left\{ 16.59158 - \frac{3,643.31}{318.15 - 33.424} \right\} = 44.51 \text{ kPa}$$

$$P_2^{sat} = \exp \left\{ 14.25326 - \frac{2,665.34}{318.15 - 53.424} \right\} = 65.64 \text{ kPa}$$

$$P = (0.25)(1.8640)(44.51 \text{ kPa}) + (0.75)(1.0716)(65.64 \text{ kPa})$$

$P = 73.5 \text{ kPa}$

$$y_1 = \frac{X_1 \gamma_1 P_1^{sat}}{P} = \frac{(0.25)(1.8640)(44.51 \text{ kPa})}{(73.5 \text{ kPa})} = \boxed{0.282 = y_1}$$

$$y_2 = 1 - y_1 = \boxed{0.718 = y_2}$$

(6) Calculate $P + x_i$ for $T = 318.15K +$ $y_1 = 0.60$
 $\Rightarrow y_2 = 0.40$
 $\delta_i = f(x_i) \Rightarrow$ PROBLEM (NEED TO ITERATE)

PROCEDURE: 1) GUESS VALUES FOR δ_i

- 2) Calculate P
- 3) Calculate x_i
- 4) Calculate δ_i
- 5) Repeat steps 2-4 until no change in δ_i

EQUATIONS:

$$P = \frac{1}{\sum_i \left(\frac{y_i}{\delta_i P_i^{sat}} \right)}$$

$$P = \frac{1}{\frac{0.6}{44.51 \delta_1} + \frac{0.4}{65.64 \delta_2}}$$

$$x_1 = \frac{0.6 P}{44.51 \delta_1}$$

$$x_2 = 1 - x_1$$

$$\delta_1 = \exp\{1.1071 x_2^2\}$$

$$\delta_2 = \exp\{1.1071 x_1^2\}$$

GUESSES

δ_1	δ_2	P	x_1	x_2
1	1	51.09	0.689	0.311
1.113	1.691	63.63	0.771	0.229
1.060	1.931	63.00	0.801	0.199
1.045	2.035	62.90	0.811	0.189
1.040	2.071	62.88	0.815	0.185
1.039	2.086	62.91	0.816	0.184
1.038	2.090	62.88	0.817	0.183

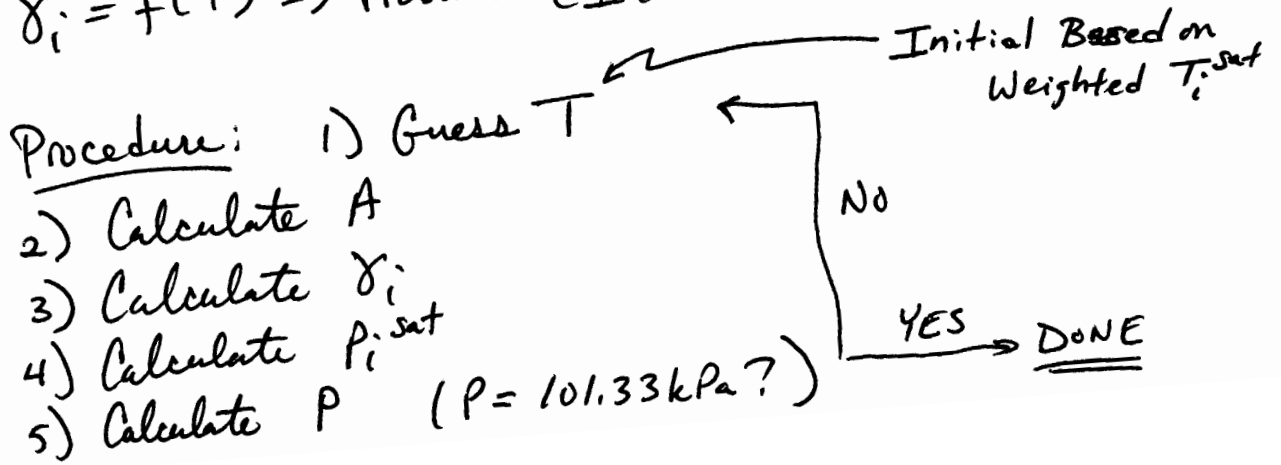
Pretty good.

$P = 62.88 \text{ kPa}$

$x_1 = 0.817$

$x_2 = 0.183$

(c) Calculate $T + y_i$ Given $P = 101.33 \text{ kPa} + x_1 = 0.85$
 $\delta_i = f(T) \Rightarrow$ Problem. (Iterative Procedure)



T	A	γ_1	γ_2	P_1^{sat}	P_2^{sat}	P
336.6	1.011	1.023	2.076	96.97	126.50	123.7
331.0	1.040	1.024	2.120	77.35	104.62	100.6
331.1	1.039	1.024	2.118	77.66	104.98	100.9
331.2	1.039	1.024	2.118	77.98	105.35	101.3

$$T_1^{\text{sat}} = \frac{3,643.31}{16.59158 - \ln(101.33)} + 33.424 = 337.7 \text{ K}$$

$$T_2^{\text{sat}} = \frac{2665.54}{14.25326 - \ln(101.33)} + 53.424 = 330.1 \text{ K}$$

$$\text{Initial Guess } T = 0.85(337.7) + 0.15(330.1) = 336.6 \text{ K}$$

$$\Rightarrow \boxed{T = 331.2 \text{ K}}$$

$$y_1 = \frac{(0.85)(1.024)(77.98 \text{ kPa})}{(101.3 \text{ kPa})} = \boxed{0.67 = y_1}$$

$$y_2 = 1 - 0.67 \Rightarrow \boxed{y_2 = 0.33}$$

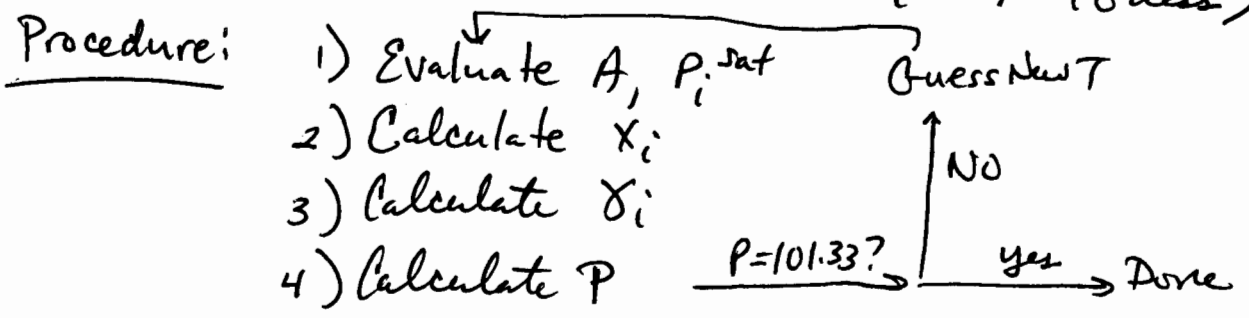
(d) Calculate T & x_i Given $P=101.33 \text{ kPa}$ & $y_1=0.40$

\Rightarrow Another headache...

$T_1^{sat} = 337.7 \text{ K}$ $T_2^{sat} = 330.1 \text{ K}$

Initial Guess: $T = 0.4(337.7) + (0.6)(330.1)$
 $T = 333.1 \text{ K}$

Don't know $x_i \Rightarrow$ Assume $\gamma_i = 1$ (Guess)



$T = 333.1 \text{ K}$ & $\gamma_1 = 1$, $\gamma_2 = 1$

$\Rightarrow A = 1.029$

$\Rightarrow P_1^{sat} = 84.27 \text{ kPa}$ $P_2^{sat} = 112.44 \text{ kPa}$

$\Rightarrow x_1 = 0.481$ $x_2 = 0.519$

$\Rightarrow \gamma_1 = 1.319$ $\gamma_2 = 1.269$

$\Rightarrow P = 127.52 \text{ kPa} \neq 101.33 \text{ kPa}$
(Lower T)

$$T = 328 \text{ K}$$

$$\gamma_1 = 1.319$$

$$\gamma_2 = 1.269$$

$$\Rightarrow A = 1.056$$

$$\Rightarrow P_1^{\text{sat}} = 68.28 \text{ kPa}$$

$$P_2^{\text{sat}} = 94.20 \text{ kPa}$$

$$\Rightarrow X_1 = 0.450$$

$$X_2 = 0.550$$

$$\Rightarrow \gamma_1 = 1.376$$

$$\gamma_2 = 1.238$$

$$\Rightarrow P = 106.42 \text{ kPa}$$

$$\neq 101.33 \text{ kPa}$$

(Lower T)

$$T = 327 \text{ K}$$

$$\gamma_1 = 1.376$$

$$\gamma_2 = 1.269$$

$$\Rightarrow A = 1.061$$

$$\Rightarrow P_1^{\text{sat}} = 65.46 \text{ kPa}$$

$$P_2^{\text{sat}} = 90.92 \text{ kPa}$$

$$\Rightarrow X_1 = 0.450$$

$$X_2 = 0.550$$

$$\Rightarrow \gamma_1 = 1.378$$

$$\gamma_2 = 1.240$$

$$\Rightarrow P = 102.60 \text{ kPa} \neq 101.33 \text{ kPa}$$

(Lower T)

$T = 326\text{K}$

$\gamma_1 = 1.378$

$\gamma_2 = 1.240$

$\Rightarrow A = 1.066$

$\Rightarrow P_1^{sat} = 62.74\text{ kPa}$

$P_2^{sat} = 87.72\text{ kPa}$

$\Rightarrow X_1 = 0.469$

$X_2 = 0.531$

$\Rightarrow \gamma_1 = 1.351$

$\gamma_2 = 1.264$

$\Rightarrow P = 98.63\text{ kPa} \neq 101.3\text{ kPa}$
(Increase T)

$T = 326.7\text{K}$

$\gamma_1 = 1.351$

$\gamma_2 = 1.264$

$\Rightarrow A = 1.062$

$\Rightarrow P_1^{sat} = 64.64\text{ kPa}$

$P_2^{sat} = 89.95\text{ kPa}$

$\Rightarrow X_1 = 0.464$

$X_2 = 0.536$

$\Rightarrow \gamma_1 = 1.357$

$\gamma_2 = 1.257$

$\Rightarrow P = 101.3\text{ kPa}$

$\Rightarrow X_1 = 0.464$
 $X_2 = 0.536$

10.6 VLE FROM K-VALUE CORRELATIONS

$$K_i \equiv \frac{y_i}{x_i}$$

K_i from Raoult's Law or Modified Raoult's Law.

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

← RAULT'S LAW
(IDEAL GAS/
IDEAL LIQUID)

$$K_i = \frac{\gamma_i P_i^{sat}}{P}$$

← MODIFIED RAULT'S
LAW
(IDEAL GAS/NON-IDEAL
LIQUID)

DePriester CHARTS (BASED ON RAULT'S LAW)

(Fig. 10.13 + 10.14)

WHY? $K_i = f(T, P)$ only.

(for RAULT'S LAW)

EXAMPLE 10.4 FOR A MIXTURE OF 10 mol% CH₄, 20 mol% C₂H₆, AND 70 mol% C₃H₈ @ 50°F,

DETERMINE:

- (a) Dewpoint Pressure
- (b) Bubblepoint Pressure

K-values are given in Figure 10.13.

(a) Dewpoint

⇒ Essentially all vapor

⇒ Overall composition $\cong y_i$

Species	y _i	P = 100 psia		P = 150 psia	
		K _i	y _i /K _i	K _i	y _i /K _i
Methane	0.1	20	0.005	13.3	0.008
Ethane	0.2	3.2	0.063	2.2	0.091
Propane	0.7	0.92	0.761	0.66	1.061

$$\sum_i x_i = \sum_i \frac{y_i}{K_i} = 1$$

0.829
 ↑
 Higher P

1.16
 ↑
 Lower P.

FROM LINEAR INTERPOLATION, GUESS $P \approx 126$ psia

	y_i	K_i	y_i/K_i
Methane	0.1	16	0.006
Ethane	0.2	2.7	0.074
Propane	0.7	0.78	0.897

0.977 ← NOT BAD

(Less than 3% error.)

(b) Bubble point

⇒ Essentially all liquid. (should need high pressure)

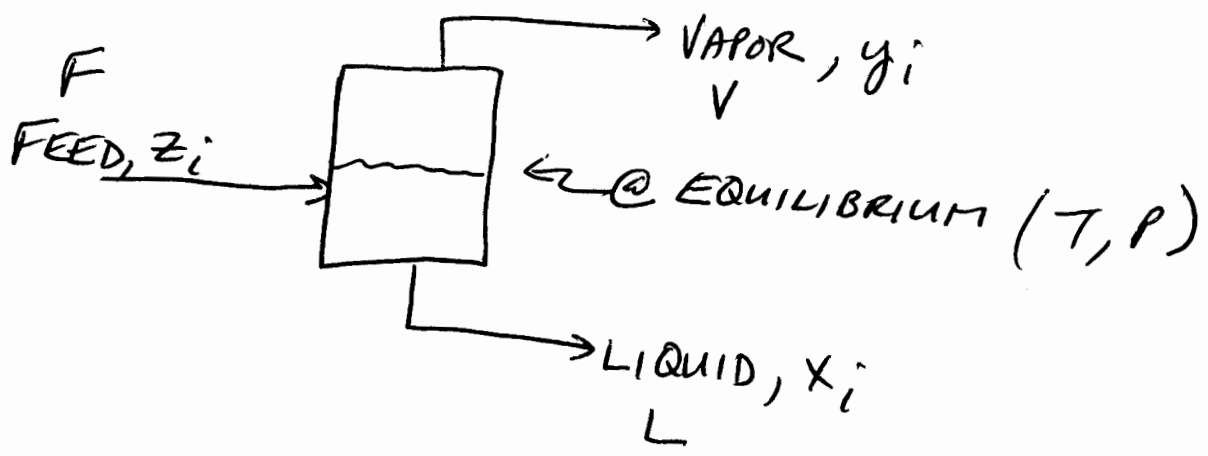
⇒ Overall composition $\cong X_i$

Species	X_i	$P = 500$ psia			$P = 400$ psia		$P = 385$ psia	
		K_i	$K_i X_i$		K_i	$K_i X_i$	K_i	$K_i X_i$
CH_4	0.1	4.2	0.42	5.1	0.51	5.3	0.53	
C_2H_6	0.2	0.9	0.18	1.0	0.2	1.05	0.21	
C_3H_8	0.7	0.27	0.189	0.31	0.217	0.32	0.224	
		0.789		0.927		0.964		
		decrease P		Slightly lower P		Less than 4% error		

Next, Flash Calculations.

FLASH CALCULATIONS

SINGLE STAGE SEPARATION BASED ON VLE,



WHAT DO WE USUALLY KNOW?

$$F, z_i, T, P$$

WHAT ARE LOOKING FOR?

$$V, L, y_i, x_i$$

EQUATIONS:

$$\sum x_i = 1$$

$$F = L + V$$

$$\sum y_i = 1$$

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

$$y_i = K_i x_i$$

FOR IDEAL GAS / IDEAL LIQUID

$$K_i = \frac{P_i^{sat}}{P} \quad (+ P_i^{sat} = f(T) \text{ only})$$

WE CAN COMBINE EQUATIONS TO GET ONE VARIABLE IN TERMS OF KNOWN.

OVERALL: $F = L + V \Rightarrow L = F - V$

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

SUBSTITUTE:

$$y_i = \frac{1}{V} [z_i F - x_i (F - V)]$$

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

PHASE EQUILIBRIA:

SUBSTITUTE,

$$\left[V y_i = z_i F - \frac{y_i}{K_i} (F - V) \right] \frac{K_i}{F}$$

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

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

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

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

But $\sum_i y_i = 1$

$$\Rightarrow 1 = \sum_i \left(\frac{z_i K_i}{\left[1 + \frac{V}{F} (K_i - 1) \right]} \right)$$

EXAMPLE 10.5 The system acetone (1) / acetonitrile (2) / nitromethane (3) at 80°C and 110 kPa has the overall composition, $z_1 = 0.45$, $z_2 = 0.35$, and $z_3 = 0.20$. Assuming that Raoult's Law is appropriate to this system, determine L , V , x_i , and y_i . The vapor pressures of the pure species at 80°C are:

$$P_1^{\text{sat}} = 195.75\text{ kPa}$$

$$P_2^{\text{sat}} = 97.84\text{ kPa}$$

$$P_3^{\text{sat}} = 50.32\text{ kPa}$$

SOLUTION:

STEP 1: BUBBLE P

ALL LIQUID OUT SO $z_i = x_i$

$$P_{\text{BUBBLE}} = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} + x_3 P_3^{\text{sat}}$$

$$= (0.45)(195.75) + (0.35)(97.84) + (0.2)(50.32)$$

$$P_{\text{BUBBLE}} = 132.4 \text{ kPa}$$

STEP 2: DEW P

ALL VAPOR OUT SO $z_i = y_i$

$$P_{\text{DEW}} = \frac{1}{\frac{y_1}{P_1^{\text{sat}}} + \frac{y_2}{P_2^{\text{sat}}} + \frac{y_3}{P_3^{\text{sat}}}}$$

$$= \frac{1}{\frac{0.45}{195.75} + \frac{0.35}{97.84} + \frac{0.2}{50.32}}$$

$$P_{\text{DEW}} = 101.5 \text{ kPa}$$

Why calculate P_{BUBBLE} + P_{DEW} ?

SET UPPER + LOW BOUNDS ON P.

(ONLY HOLDS FOR IDEAL GAS + IDEAL LIQUID)

$$P = 110 \text{ kPa} \Rightarrow 2 \text{ PHASE} \Rightarrow \underline{\underline{\text{FLASH}}}$$

$$K_i = \frac{P_i^{\text{sat}}}{P} \quad (\text{RAULT'S LAW})$$

$$K_1 = \frac{195.75}{110} = 1.7795$$

CHOOSE BASIS:

$$F = 1 \text{ mol}$$

$$K_2 = \frac{97.84}{110} = 0.8895$$

$$K_3 = \frac{50.32}{110} = 0.4575$$

NOW, SUBSTITUTE INTO FLASH EQUATION,

$$1 = \frac{(0.45)(1.7795)}{1 + \frac{V}{1}(1.7795 - 1)} + \frac{(0.35)(0.8895)}{1 + \frac{V}{1}(0.8895 - 1)} + \frac{(0.20)(0.4575)}{1 + \frac{V}{1}(0.4575 - 1)}$$

SOLVER:

$$V = 0.7367 \text{ mol}$$

$$L = F - V = 1 - 0.7367$$

$$L = 0.2633 \text{ mol}$$

$$y_1 = \frac{(0.45)(1.7795)}{1 + 0.7367(1.7795 - 1)} \Rightarrow y_1 = 0.5087$$

$$y_2 = \frac{(0.35)(0.8895)}{1 + 0.7367(0.8895 - 1)} \Rightarrow y_2 = 0.3389$$

$$y_3 = \frac{(0.20)(0.4575)}{1 + 0.7367(0.4575 - 1)} \Rightarrow y_3 = 0.1524$$

DOUBLE CHECK: $\sum y_i = 1$ ✓

FROM K_i , CALCULATE x_i

$$x_1 = 0.2859$$

$$x_2 = 0.3810$$

$$x_3 = 0.3331$$

DOUBLE CHECK:
 $\sum x_i = 1$ ✓