

SEPARATION PROCESSES :CHAPTER 2: THERMODYNAMICS

SEPARATIONS

EQUILIBRIUM

(THERMODYNAMICS)

RATE-BASED

(MASS TRANSFER)

→ EQNS OF STATE

→ DIFFUSIVITIES

→ IDEAL / NON-IDEAL

→ SOLUBILITIES

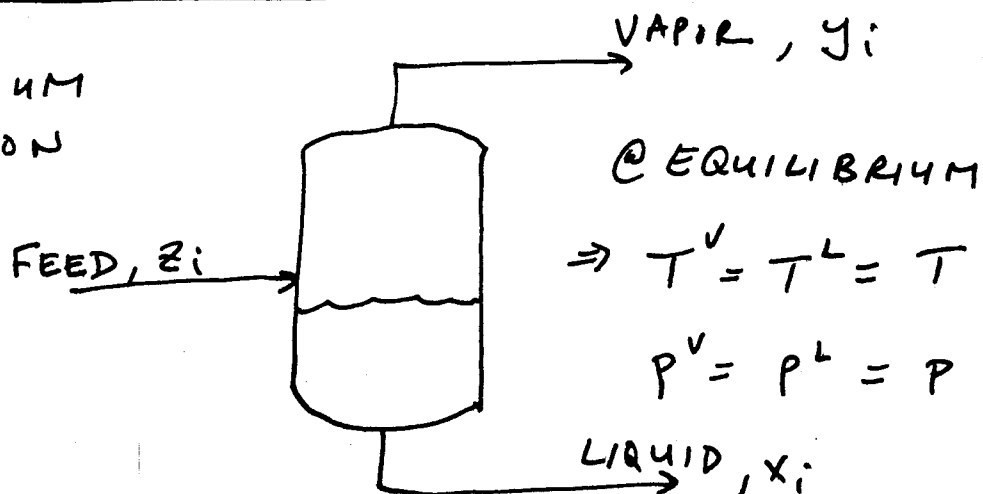
→ NO DRIVING FORCE

→ MASS TRANSFER
COEFFICIENTS

→ ACTIVITY COEFFICIENTS

e.g., DISTILLATION

e.g., ABSORPTION

EQUILIBRIUM
OPERATION

FOR VAPOR-LIQUID EQUILIBRIUM (VLE) ②

$z \equiv$ feed mole fraction

$y \equiv$ vapor mole fraction

$x \equiv$ liquid mole fraction

HOW DO WE RELATE y & x ?

$$\boxed{y_i = K_i x_i} \leftarrow \text{@ EQUILIBRIUM}$$

THERMODYNAMICS
IS IN HERE

VLE:

① IDEAL GAS / IDEAL LIQUID

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

RAOULT'S LAW

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

EXAMPLE: SYSTEM OF ALKANES

$$\Rightarrow x_i^\alpha \gamma_i^\alpha = x_i^\beta \gamma_i^\beta$$

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$$K_i =$$

If ideal, do you get a separation?

WHERE DO THESE EXPRESSIONS COME FROM?

PHASE EQUILIBRIUM

⇒ Defined by

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$$

↑
Chemical Potential

WHAT IS A CHEMICAL POTENTIAL?

→ ABSTRACT (CAN'T REALLY MEASURE)

→ THINK OF AS AN ESCAPING TENDENCY

→ HIGHER μ ⇒ BETTER CHANCE TO ESCAPE
(OR CHANGE PHASE)

$$\mu_i \equiv \left[\frac{\partial (nG)}{\partial n_i} \right]_{P, T, n_j}$$

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NOTICE:

$$G = f(P, T, n_i)$$

$$\Rightarrow \mu = f(\underbrace{P, T, n_i})$$

ALL THINGS WE CAN MODIFY
AND MEASURE

P & T GIVE A ENERGY TO SYSTEM
US WAYS
TO ADD

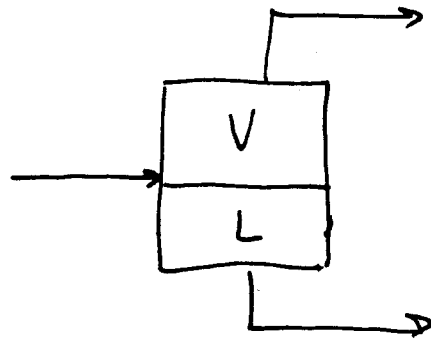
n_i LETS US CHANGE CONCENTRATION

WE'D LIKE TO START FROM HERE AND
GET TO A USABLE EXPRESSION (E.G., RAULT'S LAW)

RAOULT'S LAW : DERIVATION

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⇒ IDEAL GAS, IDEAL LIQUID



ⓐ EQUILIBRIUM
(VLE)

$$\Rightarrow \mu_i^V = \mu_i^L$$

$$\mu_i^V = G_i^{ig} + RT \ln y_i$$

$$\mu_i^L = G_i^l + RT \ln x_i$$

} Note strong dependence on composition

$$\begin{array}{ccc} G_i^{ig} + RT \ln y_i & = & G_i^l + RT \ln x_i \\ \uparrow & & \uparrow \\ \text{Pure} & & \text{Pure} \\ \text{Species} & & \text{Species} \end{array}$$

$$\Rightarrow G = f(T, P) \text{ only}$$

$$RT \ln y_i - RT \ln x_i = G_i^l(T, P) - G_i^{ig}(T, P) \quad (7)$$

ASIDE: $G_i^l(T, P)$

KNOW LIQUID PROPERTIES NOT STRONG FUNCTION OF PRESSURE

WHY?

$$\Rightarrow G_i^l(T, P) = G_i^l(T, P_i^{\text{sat}})$$

ASIDE: $G_i^{ig}(T, P)$

$$G_i^{ig}(T, P) = V^{ig} dP - S^{ig} dT \quad \text{at } T \text{ constant}$$

WHY NOT CANCEL OUT dP term?

INTEGRATE FROM $P \rightarrow P_i^{\text{sat}}$ @ constant T

$$G_i^{ig}(T, P_i^{\text{sat}}) - G_i^{ig}(T, P) = \int_P^{P_i^{\text{sat}}} \frac{RT}{P} dP$$

ideal gas law

$$= RT \int_P^{P_i^{sat}} \frac{dP}{P}$$

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$$G_i^{ig}(T, P_i^{sat}) - G_i^{ig}(T, P) = RT \ln \frac{P_i^{sat}}{P}$$

$$\Rightarrow G_i^{ig}(T, P) = G_i^{ig}(T, P_i^{sat}) - RT \ln \frac{P_i^{sat}}{P}$$

BACK TO DERIVATION ...

$$RT \ln \left(\frac{y_i}{x_i} \right) = G_i^l(T, P_i^{sat}) - \left\{ G_i^{ig}(T, P_i^{sat}) - RT \ln \frac{P_i^{sat}}{P} \right\}$$

BUT, FOR PURE
COMPONENT @ EQUILIBRIUM,

$$G_i^{\alpha} = G_i^{\beta}$$

$$\Rightarrow G_i^l(T, P_i^{sat}) = G_i^{ig}(T, P_i^{sat})$$

$$\Rightarrow RT \ln \frac{y_i}{x_i} = RT \ln \frac{P_i^{sat}}{P}$$

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

$$\Rightarrow \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} \quad \text{or}$$

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

NOTES: x_i & y_i are mole fractions
 P is total system pressure
 P_i^{sat} is saturation pressure of pure component "i" @ mixture T

→ $P_i^{sat} = f(T)$ only. Get from Antoine Equation

$$\ln P_i^{sat} = A - \frac{B}{T+C}$$

Coefficients $A, B,$ and C from literature

* RAOULT'S LAW FOR IDEAL GAS/IDEAL LIQUID *

WHAT IF NON-IDEAL?

IG/NIL: MODIFIED RAOULT'S LAW

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

γ_i from ACTIVITY COEFFICIENT MODELS

P_i^{sat} from ANTOINE EQUATION

NIG/NIL:

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

$\bar{\Phi}_i$ from equation of state

γ_i from activity coefficient models

P_i^{sat} from Antoine Equation

NIL/NIL: (for LLE)

$$x_i^{\alpha} \gamma_i^{\alpha} = x_i^{\beta} \gamma_i^{\beta}$$

$\gamma_i^{\alpha}, \gamma_i^{\beta}$ from activity coefficient model

PHASE DIAGRAMS:

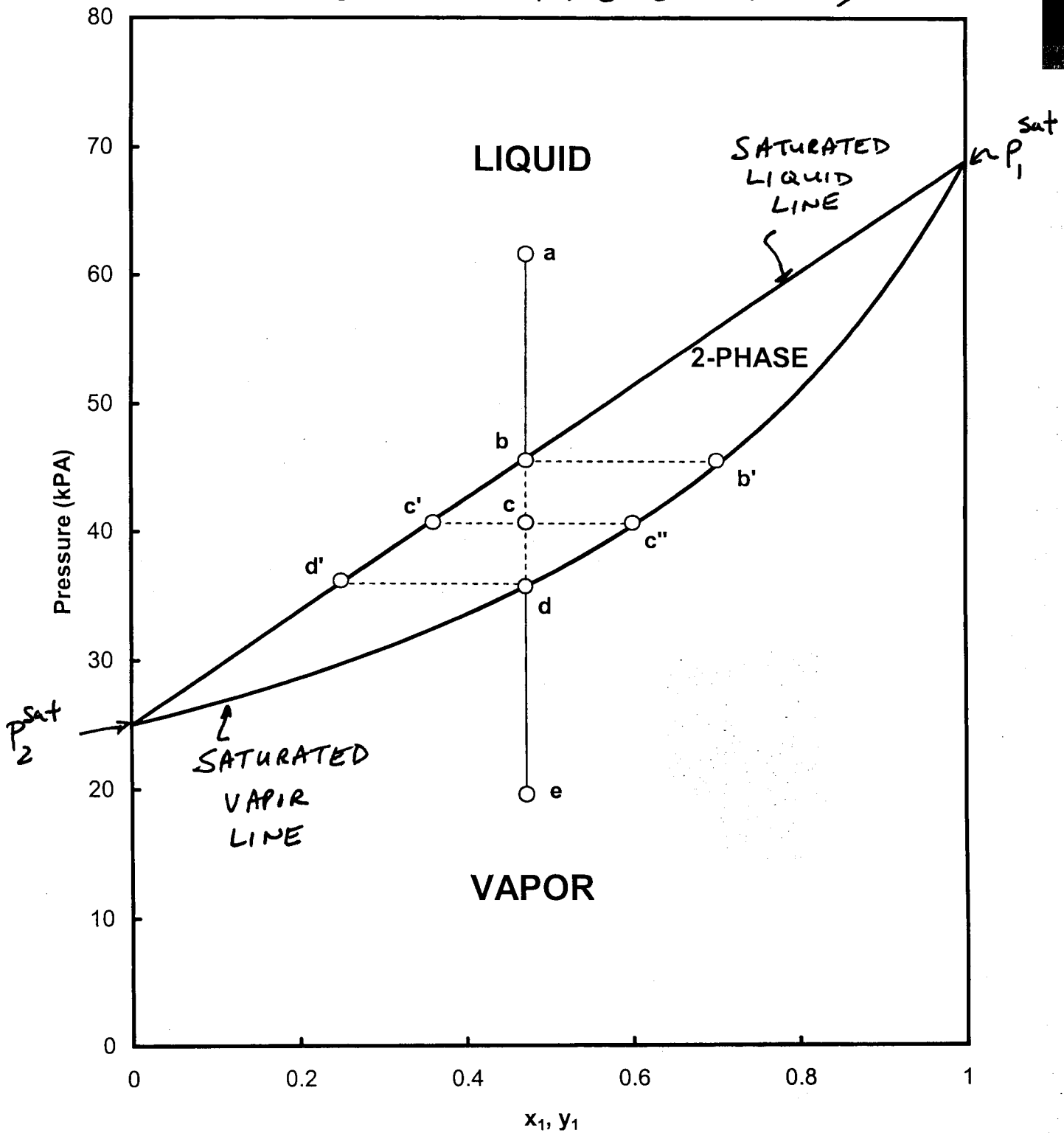
① IDEAL GAS / IDEAL LIQUID (BINARY SYSTEM)

NEED: RAULT'S LAW EXPRESSIONS

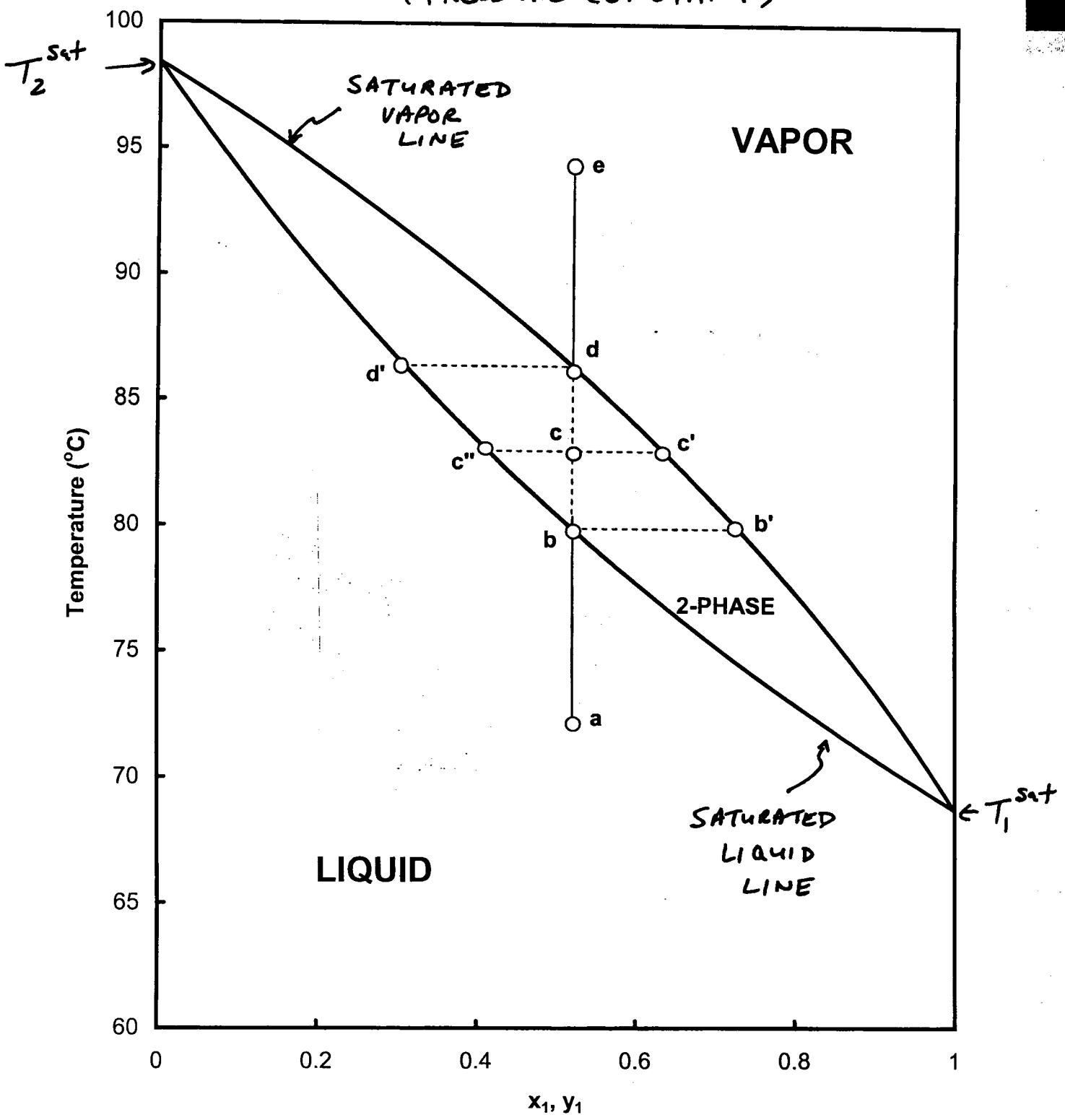
SUMMATIONS (MOLE FRACTIONS)

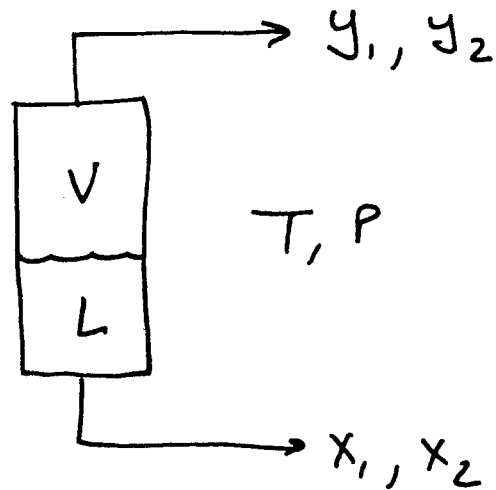
PXY Phase Diagram for n-Hexane (1) and n-Heptane (2)

(TEMPERATURE CONSTANT)



TXY Phase Diagram for n-Hexane (1) and n-Heptane (2)
(PRESSURE CONSTANT)





<u>POINT</u>	<u>DESCRIPTION</u>
a	SUBCOOLED LIQUID, ONE PHASE
b	BUBBLE POINT, $x_1 = z_1$
b'	BUBBLE POINT VAPOR COMPOSITION (BUT NO VAPOR YET)
c	TWO-PHASE REGION
c'	x_1 for PRESSURE @ c
c''	y_1 for PRESSURE @ c
d	DEW POINT, $y_1 = z_1$

d' DEW POINT LIQUID COMPOSITION
(BUT NO LIQUID PHASE)

e SUPER-HEATED VAPOR, ONE PHASE

NOTE: AT POINTS A & E, NO SEPARATION

WHY? ONLY ONE PHASE

HOW TO GENERATE PXY DIAGRAMS (IG/IL):

T IS CONSTANT

$P_i^{\text{sat}} = f(T)$ only, so can calculate P_i^{sat} immediately.

BINARY SYSTEM:

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

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

$$x_1 + x_2 = 1 \quad (3)$$

$$y_1 + y_2 = 1 \quad (4)$$

COMBINE (1) + (2)

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

$$P = x_1 P_1^{\text{sat}} + (1 - x_1) P_2^{\text{sat}}$$

$$P = P_2^{\text{sat}} + (P_1^{\text{sat}} - P_2^{\text{sat}}) x_1$$

← SATURATED
LIQUID LINE

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

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

PLOT (y_1, P) FOR
SATURATED VAPOR LINE

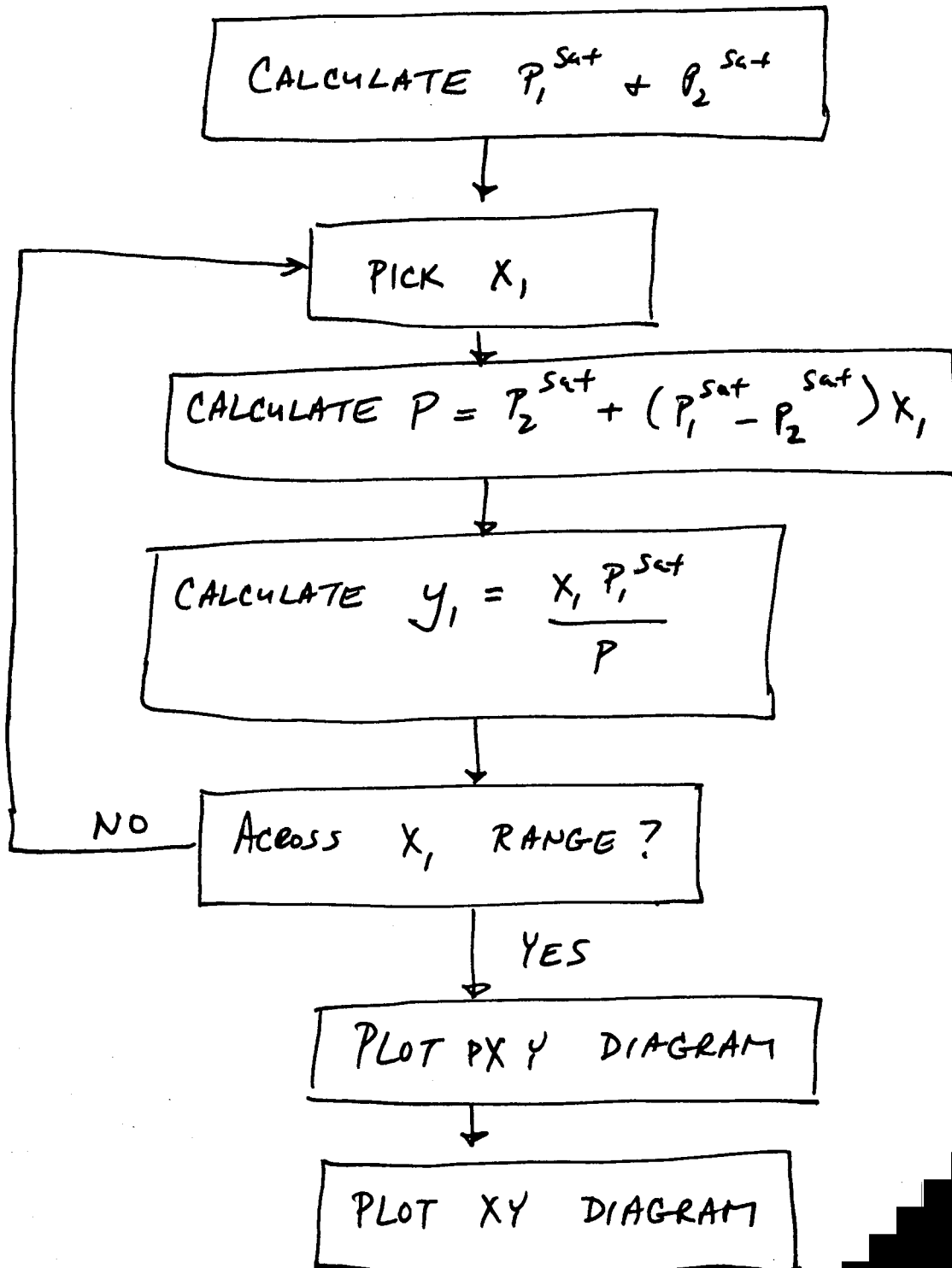
NOTES:

- BOTH LINES TERMINATE AT PURE COMPONENTS $(x_1 = 1, y_1 = 1)$ SO ENDPOINTS ARE P_2^{sat} & P_1^{sat}
- SATURATED LIQUID LINE IS STRAIGHT
FOR $\neq G/\neq L$

PXY (IDEAL GAS / IDEAL LIQUID)

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



HOW TO GENERATE TXY DIAGRAMS (IG/IL)

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P is constant

At endpoints, $P = P_i^{\text{sat}}$, so calculate T_i^{sat} at endpoints.

Then, for any T... calculate P_i^{sat} , then

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

$$\Rightarrow X_1 = \frac{P - P_2^{\text{sat}}}{P_1^{\text{sat}} - P_2^{\text{sat}}}$$

$$y_1 = \frac{X_1 P_1^{\text{sat}}}{P}$$

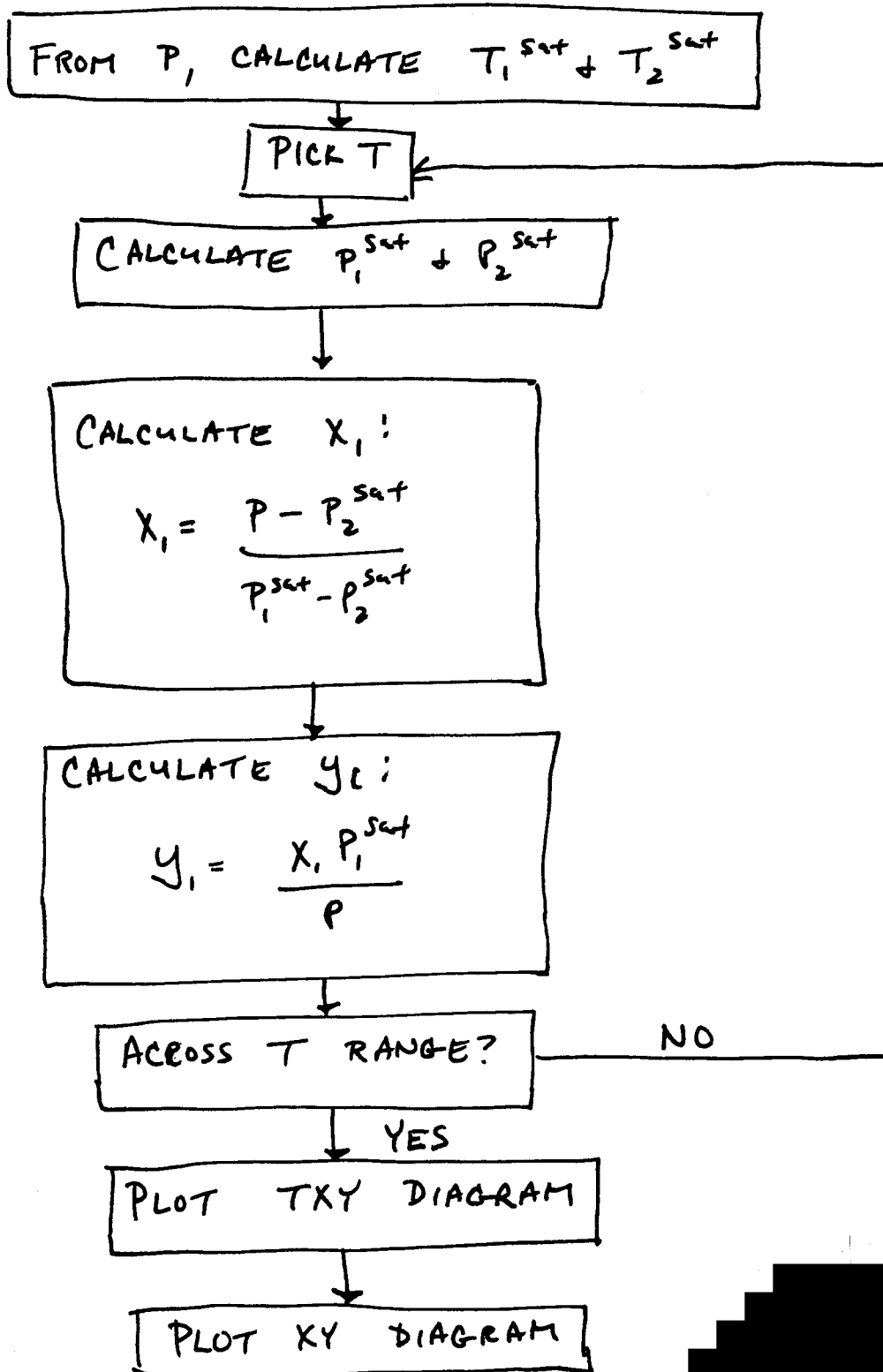
NOTES:

- PLOT (X_1, T) FOR SATURATED LIQUID LINE
- PLOT (y_1, T) FOR SATURATED VAPOR LINE
- RECALL THAT MOST INDUSTRIAL SEPARATIONS AT SET PRESSURE, SO TXY DATA MOST COMMONLY USED FOR DESIGN.

TXY (IDEAL GAS/IDEAL LIQUID)

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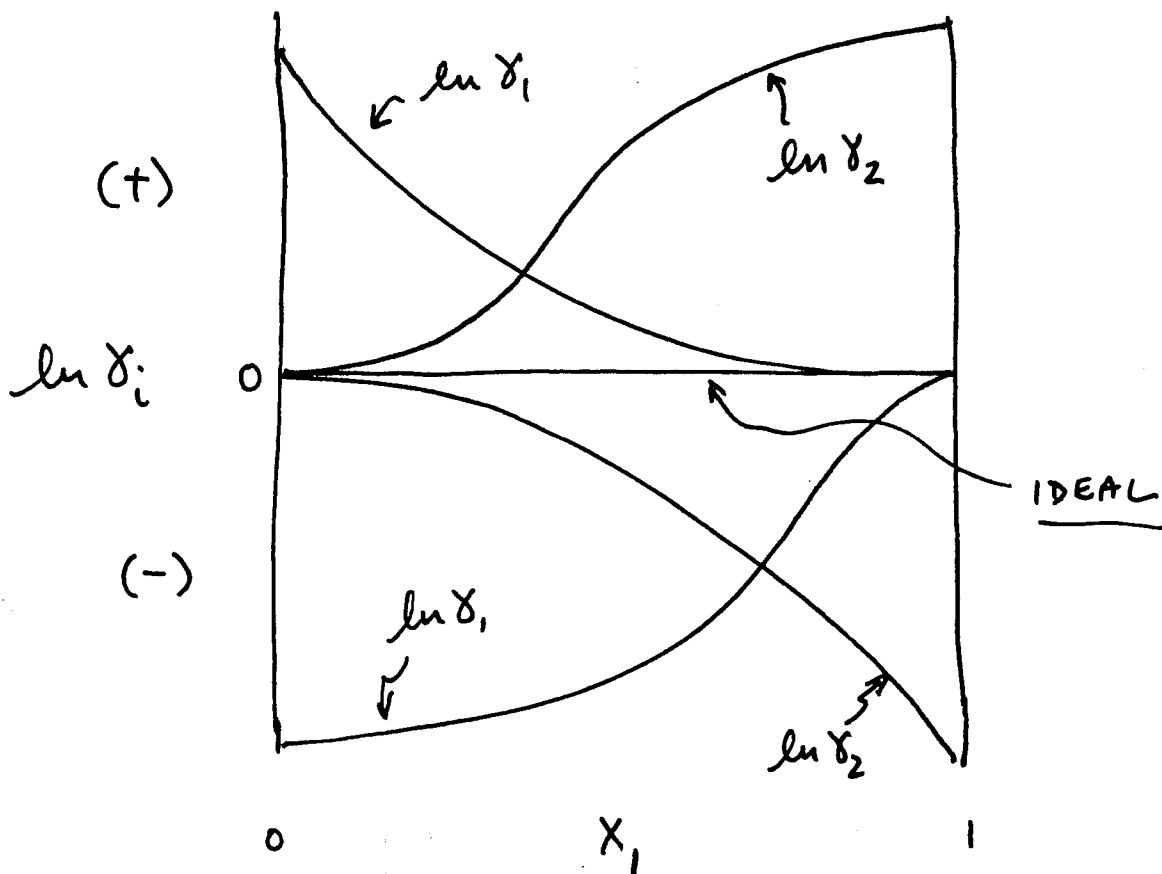
- RAULT'S LAW APPLIES
- ANTOINE EQUATION FOR P_i^{sat}
- CONSTANT P



ACTIVITY COEFFICIENT MODELS :

- TYPES :
- 1) POLYNOMIAL EXPANSIONS w/ MULTIPLE, EMPIRICALLY FITTED, ADJUSTABLE PARAMETERS
 - 2) FLORY-HUGGINS : EXTENDS LATTICE THEORY TO DIFFERENT SHAPED MOLECULES
 - 3) LOCAL COMPOSITION EFFECTS TO ACCOUNT FOR NON-RANDOM MOLECULAR LEVEL DISTRIBUTION
 - 4) QUASI-CHEMICAL THAT ACCOUNT FOR MOLECULAR SIZE (AREA + VOLUME)

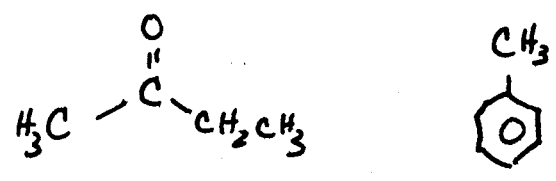
DEVIATIONS CAN BE POSITIVE OR NEGATIVE



POSITIVE DEVIATIONS:



e.g., methyl ethyl ketone / toluene



NEGATIVE DEVIATIONS:



e.g., chloroform / dioxane



VERY LARGE DEVIATIONS \Rightarrow AZEOTROPE FORMATION

GENERAL:

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

LOW PRESSURE, $\Phi_i = 1$

MOST CASES (INDUSTRIAL IMPORTANT), $\gamma_i \neq 1$

\Rightarrow MODIFIED RAULT'S LAW

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

How TO GET $\gamma_i \rightarrow$

MARGULES, VAN LAAR

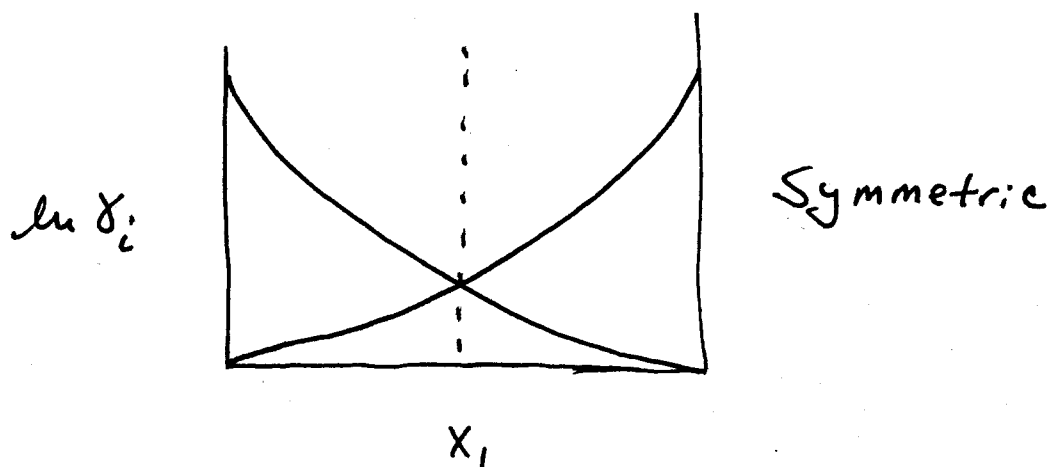
- OLDER MODELS
- BASED ON POLYNOMIAL EXPANSION + CURVE FITTING
- GOOD FOR SIMPLE MIXTURES
- GOOD FOR COMPONENTS THAT ARE SIMILAR IN NATURE + SIZE

1) MARGULES - 2 SUFFIX

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

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

one parameter: A

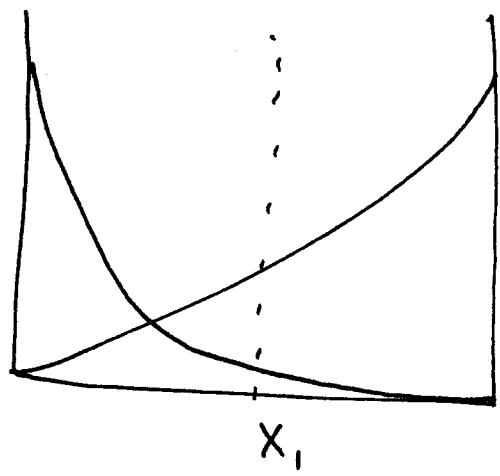


2) VAN LAAR -

$$RT \ln \gamma_1 = A \left(1 + \frac{A X_1}{B X_2} \right)^{-2}$$

$$RT \ln \gamma_2 = B \left(1 + \frac{B X_2}{A X_1} \right)^{-2}$$

$\ln \gamma_i$



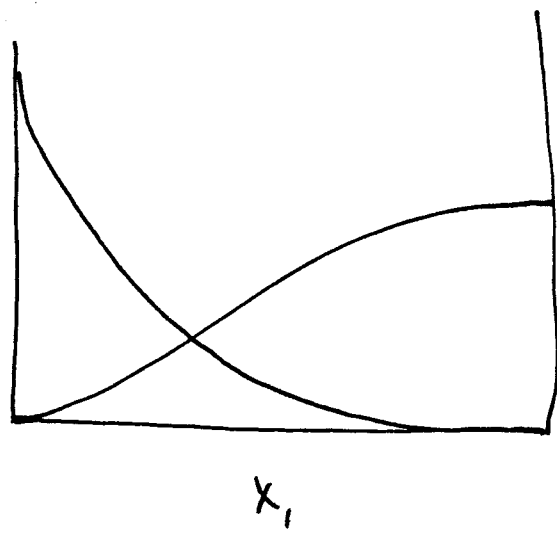
NOT
SYMMETRIC

3) MARGULES - 3 SUFFIX

$$RT \ln \gamma_1 = (A + 3B) X_2^2 - 4B X_2^3$$

$$RT \ln \gamma_2 = (A - 3B) X_1^2 + 4B X_1^3$$

$\ln \gamma_i$



4) WILSON EQUATION:

• GOOD FOR STRONGLY NON-IDEAL

e.g. alcohols + hydrocarbons

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- 2 parameter
- local composition effects
- GOOD FOR VLE, BUT NOT LLE

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right)$$

NRTL: (NON-RANDOM TWO LIQUID)

- 3 PARAMETER
- STRONGLY NON-IDEAL
- LOCAL COMPOSITIONS
- GOOD FOR VLE + LLE

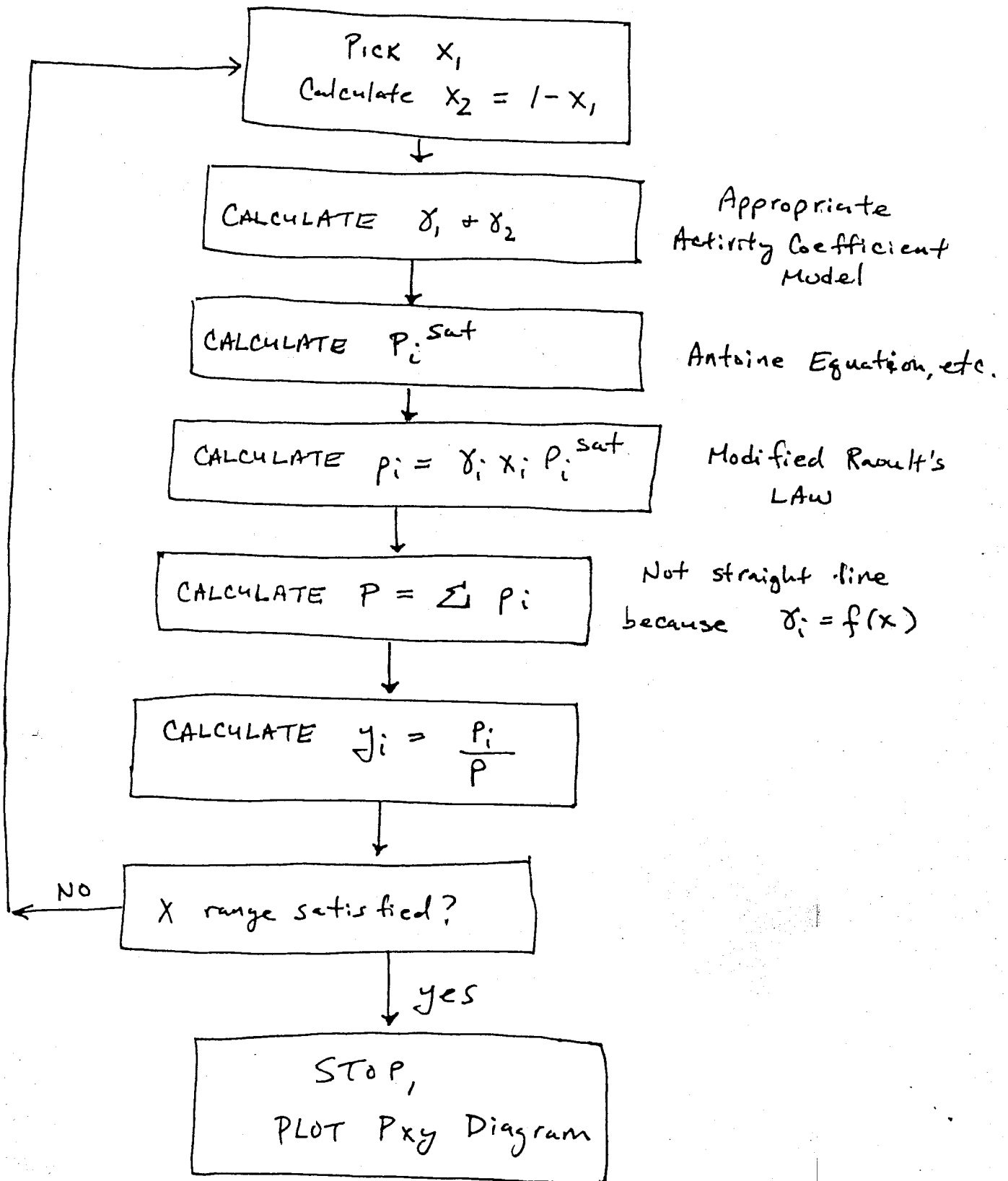
UNIQUAC: (UNIVERSAL QUASI-CHEMICAL)

- GROUP CONTRIBUTION
- VLE, LLE
- 2 parameter
- small T dependence
- Good for polymers

Pxy Diagrams (Fixed T)

(binary ideal gas / nonideal liquid)

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Txy Diagrams (Fixed P)
 (binary ideal gas / non ideal liquid)

