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CHAP. 11 + 12

SOLUTION THERMODYNAMICS

Recall from Chap. 6 (for closed system):

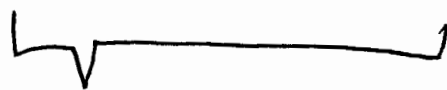
$$G = f(P, T)$$

$$d(nG) = (nV)dP - (nS)dT$$

For OPEN SYSTEM: $G = f(P, T, n_i)$

$$d(nG) = \left[\frac{\partial(nG)}{\partial P} \right]_{T, n_i} dP + \left[\frac{\partial(nG)}{\partial T} \right]_{P, n_i} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i} \right]_{P, T, n_j} dn_i$$

$$d(nG) = (nV)dP - (nS)dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i} \right]_{P, T, n_j} dn_i$$

NEW TERMCHEMICAL POTENTIAL

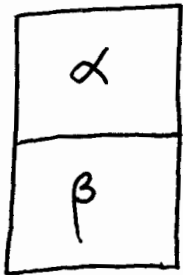
$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i} \right]_{P, T, n_j}$$

SUBSTITUTE
~

$$d(nG) = (nv)dP - (ns)dT + \sum_i \mu_i dn_i$$

↙ SOLUTION THERMO BASED ON THIS EQUATION.

HOW DOES THIS RELATE TO EQUILIBRIUM?



TWO PHASES IN EQUILIBRIUM

$$P^\alpha = P^\beta = P$$

$$T^\alpha = T^\beta = T$$

WRITE PREVIOUS EQUATION FOR EACH PHASE.

$$d(nG)^\alpha = (nv)^\alpha dP - (ns)^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$

$$+ d(nG)^\beta = (nv)^\beta dP - (ns)^\beta dT + \sum_i \mu_i^\beta dn_i^\beta$$

$$d(nG) = (nv)dP - (ns)dT + \underbrace{\sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta}_{\text{EXTRA TERMS.}}$$

CLOSED SYSTEM BALANCE

EXTRA TERMS.

↙ CAN CANCEL BASED ON CLOSED SYSTEM BALANCE

$$\therefore 0 = \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$$

BUT, OVERALL THE SYSTEM IS CLOSED, SO ANY MASS TRANSFER BETWEEN PHASES A + B IS EQUAL MAGNITUDE + OPPOSITE SIGN.

$$\underline{\text{OR}} \quad dn_i^\alpha = - dn_i^\beta \quad \underline{\text{SUBSTITUTE}}$$

$$0 = \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta (-dn_i^\alpha)$$

FACTOR OUT dn_i^α ...

$$0 = \sum_i (\mu_i^\alpha - \mu_i^\beta) \underbrace{dn_i^\alpha}_{\text{term} \neq 0}$$

So, ONLY WAY FOR RHS = 0 IS:

$$\mu_i^\alpha - \mu_i^\beta = 0 \quad \longrightarrow$$

THEREFORE, AT EQUILIBRIUM

$$\mu_i^\alpha = \mu_i^\beta \quad (i=1, 2, \dots, N)$$

Chemical potential of each component is the same in each phase.

Can't measure μ . However, can rewrite in terms of G , and $G = f(\underbrace{P, T, n_i}_{\text{measurable}})$.

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

PARTIAL MOLAR
GIBBS ENERGY

NEXT, BRING BACK TO NON-IDEAL GASES +
NON-IDEAL LIQUID.

NON-IDEAL GAS:

$$G_i^R = RT \ln \phi_i$$

Residual Gibbs for component "i" fugacity coefficient

where, $\phi_i = \frac{f_i}{P}$

fugacity component "i" System Pressure

Rewrite: $\frac{G_i^R}{RT} = \ln \phi_i$

$$\lim_{P \rightarrow 0} \left(\frac{G_i^R}{RT} \right) = \lim_{P \rightarrow 0} (\ln \phi_i) = 0$$

So, as go to IDEAL GAS,

$$\boxed{\phi_i = 1} \quad (\text{IDEAL GAS})$$

(6)

RECALL FROM CHAP. 6,

$$\frac{G_i^R}{RT} = \int_0^P (Z_i - 1) \frac{dP}{P} = \ln \phi_i$$

NITE: PVT RELATION

So, CAN USE EQUATION OF STATE TO GET ϕ_i !

Why Important?

for NON-IDEAL GAS / NON-IDEAL LIQUID

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

fugacity
coefficient

(accounts for
non-ideal gas)

Activity
coefficient

(accounts for
non-ideal liquid)

NON-IDEAL LIQUID:

$$\bar{G}_i^E = RT \ln \gamma_i$$

PARTIAL MOLAR
EXCESS GIBBS

FOR COMPONENT "i"

ACTIVITY
COEFFICIENT.

OR

$$\frac{\bar{G}_i^E}{RT} = \ln \gamma_i$$

$$\lim_{\text{interactions} \rightarrow 0} \left(\frac{\bar{G}_i^E}{RT} \right) = 0 \Rightarrow \ln \gamma_i = 0$$

OR $\gamma_i = 1$

↑
IDEAL SOLUTION.

$$\Rightarrow G_i = G_i^{id} + G_i^E = 0$$

MORE ON EXCESS PROPERTIES:

LIQUID VERSION OF RESIDUAL PROPERTIES

$$M^E \equiv M - M^{id}$$

EXCESS ACTUAL IDEAL

So,

$$RT \ln \gamma_i = \bar{G}_i - \bar{G}_i^{id}$$

But,

$$\bar{G}_i^{id} = \mu_i^{id} = G_i(T,P) + RT \ln x_i$$

SUBSTITUTE

$$RT \ln \gamma_i = \bar{G}_i - (G_i + RT \ln x_i)$$

$$RT (\ln \gamma_i + \ln x_i) = \bar{G}_i - G_i$$

$$RT \ln (\gamma_i x_i) + G_i = \bar{G}_i = \mu_i$$

WHY IMPORTANT?

IDEAL GAS : $\mu_i^{ig} = G_i^{ig} + RT \ln y_i$

IDEAL SOLUTION: $\mu_i^{id} = G_i + RT \ln x_i$

SOLUTION: $\mu_i = G_i + RT \ln(\gamma_i x_i)$

AND, AT EQUILIBRIUM:

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

All in terms of T, P, n_i (stuff we can measure!)

TWO OTHER EQUATIONS OF INTEREST
(FROM GIBBS-DUHEM)

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

$$\sum_i x_i d \ln \gamma_i = 0$$

IMPORTANT
FOR
ACTIVITY
COEFFICIENT
MODELS.

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)

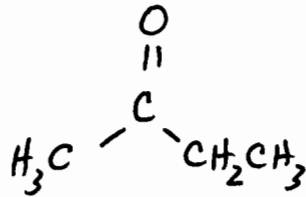
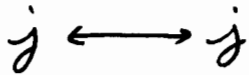
DEVIATIONS FROM IDEALITY:

CAN BE POSITIVE (+)
OR
 NEGATIVE (-)

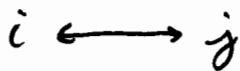
POSITIVE DEVIATIONS:



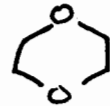
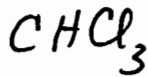
e.g., methyl ethyl ketone / toluene



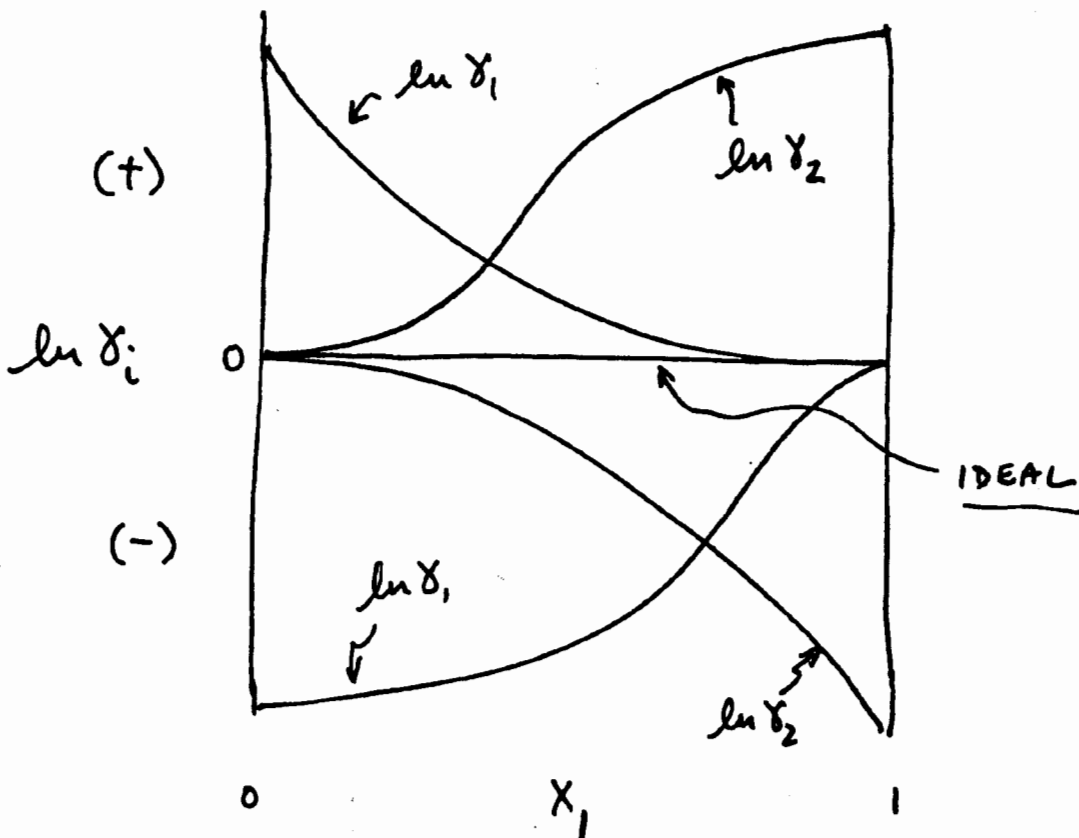
NEGATIVE DEVIATIONS:



e.g., chloroform / dioxane



VERY LARGE DEVIATIONS \Rightarrow AZEOTROPE FORMATION



How to GET γ_i ?

MARGULES, VAN LAAR

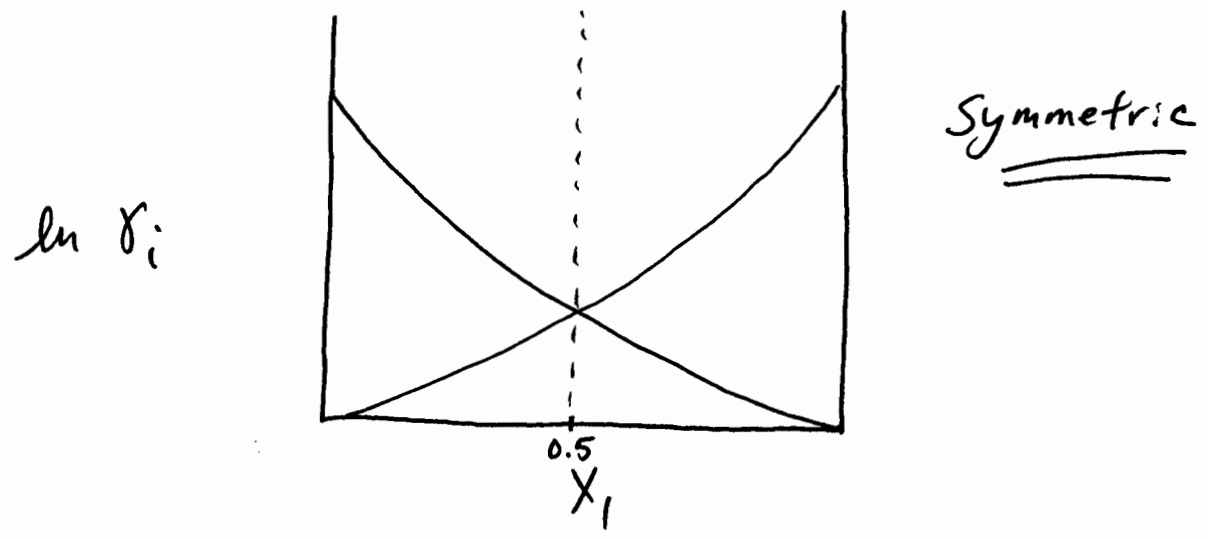
- OLDER MODELS
- BASED ON POLYNOMIAL EXPANSION + CURVE FITTING
- GOOD FOR SIMPLE MIXTURES
- GOOD FOR COMPONENTS OF SIMILAR NATURE + SIZE.

1) MARGULES - 2 SUFFIX

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

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

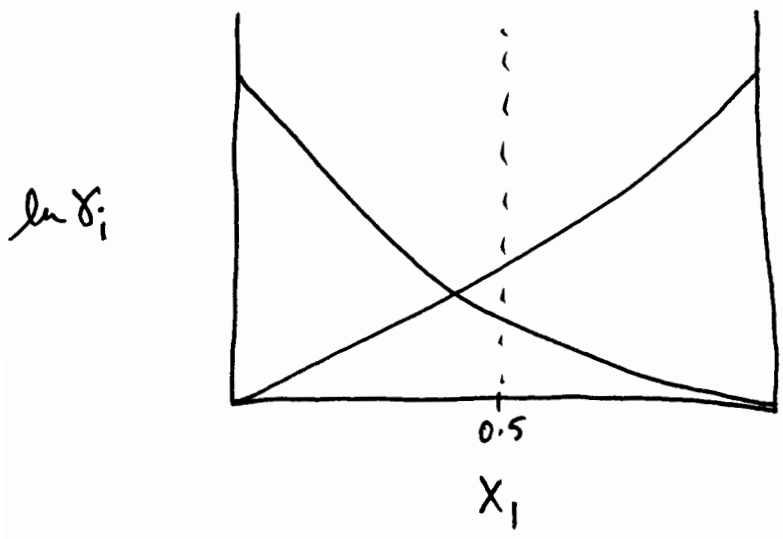
ONE PARAMETER.



2) VAN LAAR

$$RT \ln \gamma_1 = A \left(1 + \frac{Ax_1}{Bx_2} \right)^{-2}$$

$$RT \ln \gamma_2 = B \left(1 + \frac{Bx_2}{Ax_1} \right)^{-2}$$



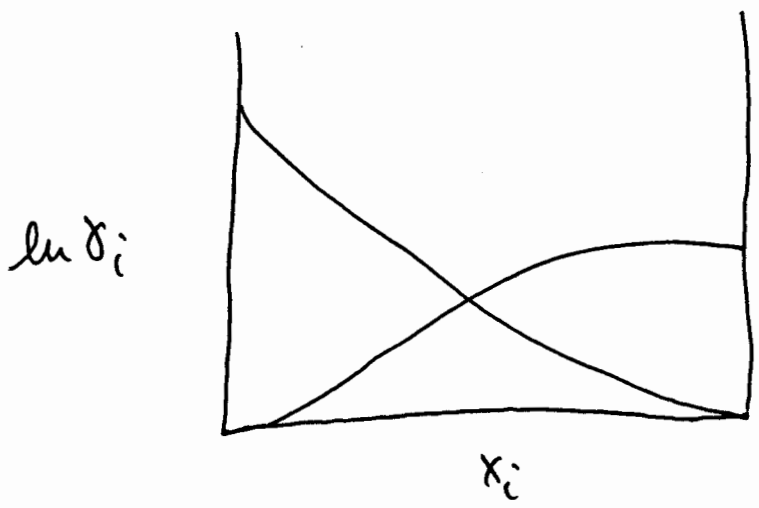
NOT SYMMETRIC

3) MARGULES - 3 SUFFIX

$$RT \ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3$$

$$RT \ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3$$

⇒ NOTE: CUBIC



POINT OF INFLECTION

⇒ VERY USEFUL

NEXT: LOCAL COMPOSITION MODELS

4) WILSON EQUATION

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

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

- GOOD FOR STRONGY NON-IDEAL (eg., alcohols + hydrocarbons)

- 2 PARAMETER

- GOOD FOR VLE, BUT NOT LLE.

NRTL: (NON-RANDOM TWO LIQUID)

- 3 PARAMETER
 - STRONGLY NON-IDEAL
 - GOOD FOR VLE + LLE.
-

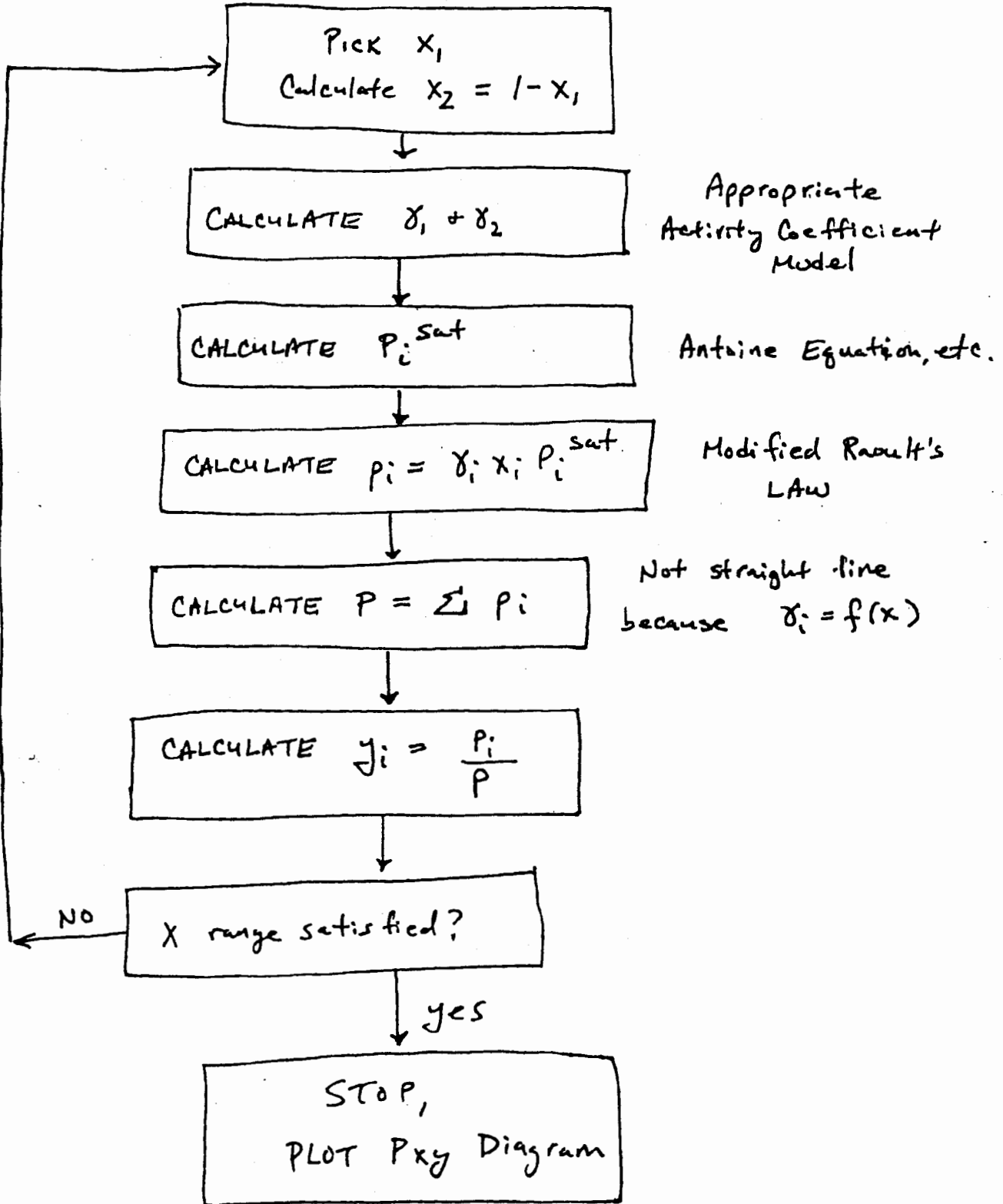
NEXT: QUASI-CHEMICAL (UNIVERSAL)

- GROUP CONTRIBUTION
 - VLE + LLE
 - 2 PARAMETER
 - SMALL TEMP. DEPENDENCE.
 - GOOD FOR POLYMERS.
-

WHY CALCULATE γ_i ?

⇒ NON-IDEAL PHASE DIAGRAMS!

Pxy Diagrams (Fixed T) (binary ideal gas / nonideal liquid)



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

