

Computer Aided Process Engineering CL303

Module-3

Vapour-Liquid and Liquid-Liquid equilibria

Module-1

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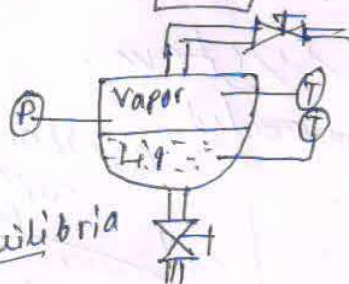
Phase Equilibria

(1)

At equilibrium there are no driving forces for energy and mass transfer.

The system shows no tendency to depart from that equilibrium state.

no influx X_i → system X → no outflux of energy, mass & momentum.



Phase equilibria

It is important in: gas-liquid absorption, distillation, liquid-liquid extraction, leaching, adsorption.

To determine x_i, y_i at equilibrium at known T, P .

To " " P, T at " " at known x_i^*, y_i^*

$$\mu_i^\alpha = \mu_i^\beta \quad \alpha \& \beta \text{ are two phases}$$

$$G_i^\alpha = G_i^\beta \quad \text{molar Gibbs free energy.}$$

$$\Rightarrow dG^\alpha = dG^\beta \quad v^\alpha dp^{\text{sat}} - s^\alpha dT = v^\beta dp^{\text{sat}} - s^\beta dT$$

$$\Rightarrow \frac{dp^{\text{sat}}}{dT} = \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} = \frac{\Delta s}{\Delta v}$$

$$ds = \frac{dq}{T}; \quad dd = dH \text{ at constant } P.$$

$$\frac{dp^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha\beta}}{T \Delta V^{\alpha\beta}} \quad \text{Clausius-Clapeyron eq.}$$

$$\ln p^{\text{sat}} = A - \frac{B}{T+C} \quad \text{from Clausius-Clapeyron eq.}$$

Antoine eqn

$$\frac{d p^{\text{sat}} / p^{\text{sat}}}{dT/T^2} = \frac{\Delta H^{\alpha\beta}}{R} = -R \left[\frac{d \ln p^{\text{sat}}}{d(1/T)} \right]$$

degree of freedom

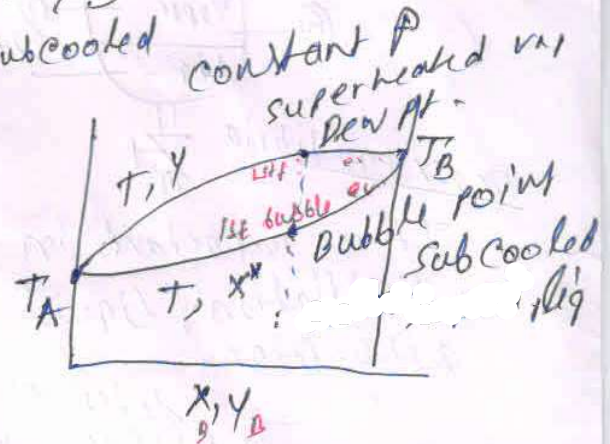
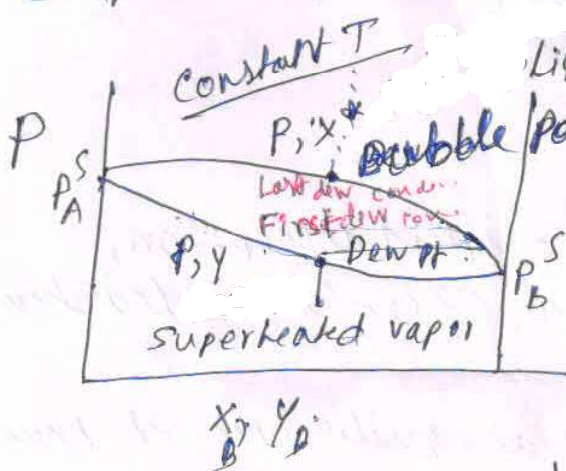
(2)

$$F = C - P + 2$$

For a two component Benzene, toluene, in vapor liquid equilibrium

$$F = 2 - P + 2 = 2, \text{ specify 2 variables}$$

For complete explanation of system,



	specified	computed
Bubble pressure	$T \text{ \& } \{x_i\}$	$P \text{ \& } \{y_i\}$
Dew "	$T \text{ \& } \{y_i\}$	$P \text{ \& } \{x_i\}$
Bubble Temp.	$P \text{ \& } \{x_i\}$	$T \text{ \& } \{y_i\}$
Dew "	$P \text{ \& } \{y_i\}$	$T \text{ \& } \{x_i\}$

at eq $f_i^L = f_i^V$

$$f_i^L = x_i \phi_i^L f_i^0$$

$$f_i^V = y_i \bar{\phi}_i^V P$$

$$y_i \bar{\phi}_i^V P = x_i \phi_i^L f_i^0$$

for ideal gas solution $\bar{\phi}_i^V = 1$

Raoult's Law ideal liquid solution $\phi_i^L = 1$ at low pressure $f_i^0 = P_i^S$
 $y_i P = x_i P_i^S$

(3)

$$y_i = x_i \frac{p_i^s}{P}$$

$$x_i = y_i \frac{P}{p_i^s}$$

$$\therefore \sum y_i = \sum x_i \frac{p_i^s}{P}$$

$$\sum x_i = \sum y_i \frac{P}{p_i^s}$$

$$\Rightarrow \sum x_i p_i^s = P \quad \text{--- (i)}$$

$$\Rightarrow \sum y_i \frac{P}{p_i^s} = 1$$

$$\ln p_i^s = A_i - \frac{B_i}{t + C_i}$$

Bubble pressure calculation P & $\{x_i\}$ given T & $\{x_i\}$

- Calculate p using $\sum x_i p_i^s = P$.
- calculate p_i^s " Antoine eqn.
- calculate $\{y_i\}$ " $y_i = x_i \frac{p_i^s}{P}$

Dew pressure calculation P & $\{x_i\}$ give T & $\{y_i\}$

- compute p from $\sum y_i \frac{P}{p_i^s} = 1$.
- " p_i^s " Antoine eqn.
- compute $\{x_i\}$ from $x_i = y_i \frac{P}{p_i^s}$

Bubble Temp calculation

Given P & $\{x_i\}$ calculate $T, \{y_i\}$

a) for a given pressure compute T_i^s

$$T_i^s = \frac{B_i}{A_i - \ln P} - C_i$$

b) Initialize bubble T as $T_b(i) = \sum_{i=1}^N x_i T_i^s$

c) using computed T calculate $\{p_i^s\}$

d) $y_i = x_i \frac{p_i^s}{P}$ calculate $\{y_i\}$

④ if $|\sum y_i - 1| < \epsilon$. $T_{\text{test}} = T_{\text{bubble}}$.

④

8) if $|\sum y_i - 1| > \epsilon$.
then $T_{\text{test}} > T_b(P)$.

$$T_{\text{new}} = T_{\text{test}} \left[\frac{\epsilon}{|\sum y_i - 1|} \right] \text{ and}$$

return to ④

if $|\sum y_i - 1| < -\epsilon$. $T_{\text{test}} < T_b(P)$.

$$T_{\text{new}} = T_{\text{test}} \frac{|\sum y_i - 1|}{\epsilon} \text{ \& return to step ④}$$

Dew temperature Given $P, \{y_i\}$ calculate T & $\{x_i\}$

a) compute T_i^S for a give pressure from Antoine

$$\text{eq. } T_i^S = \frac{B_i}{A_i - \ln P} - C_i$$

b)

Initialize dew temp. $T_{d,i} = \sum x_i T_i^S$

c) using computed T calculate $\{P_i^S\}$ $\left[\ln P_i^S = A_i - \frac{B_i}{T+C_i} \right]$

d) use $x_i = \frac{P y_i}{P_i^S}$ to calculate $\{x_i\}$

e) if $|\sum x_i - 1| < \epsilon$ then $T_{\text{test}} = T_{d,i}$

f) if $|\sum x_i - 1| > \epsilon$ then $T_{\text{test}} < T_{d,i}$, $T_{\text{new}} = \frac{\sum x_i - 1}{\epsilon}$
and return to step b).

g) if $|\sum x_i - 1| < -\epsilon$ then $T_{\text{test}} > T_{d,i}$, $T_{\text{new}} = \frac{|\sum x_i - 1|}{\epsilon}$
& return to step b)

VLE Algorithm for Low to moderate pressure

* Nonideal behaviour for both gas & liquid phases.

→ pressures away from atmospheric.

→ constituent molecules form a non-ideal liquid phase.

$$\hat{f}_i^V = f_i^L; \quad \hat{f}_i^V = y_i \hat{\phi}_i P; \quad \hat{f}_i^L = x_i \varphi_i f_i$$

$$\Rightarrow y_i \hat{\phi}_i P = x_i \varphi_i f_i \quad \text{--- (7.45)}$$

For liquid phase (fugacity function)

$$f_i(T, P) = \phi_i^{\text{sat}} p_i^{\text{sat}} \exp \left[\frac{v_i^L (P - p_i^{\text{sat}})}{RT} \right]$$

at low P: $f_i = \phi_i^S p_i^S$

$$\Rightarrow y_i \hat{\phi}_i P = x_i \varphi_i \phi_i^S p_i^S$$

$$\Rightarrow y_i \hat{\phi}_i P = x_i \varphi_i p_i^S \quad \phi_i = \frac{\hat{\phi}_i}{\phi_i^S}$$

$$\phi_i = \left(\frac{\hat{\phi}_i}{\phi_i^S} \right) \exp \left[- \frac{v_i^L (P - p_i^{\text{sat}})}{RT} \right]$$

at low pressure, $P = p_i^{\text{sat}}$. $\phi_i = \frac{\hat{\phi}_i}{\phi_i^S}$

$$\phi_i^S = \exp \left[\frac{B_{ii} p_i^S}{RT} \right]$$

$$\ln \hat{\phi}_i = \frac{P}{RT} (B_{ii} + y_j^2 \delta_{ij})$$

$$\phi_i = \exp \left[\frac{B_{ii} (P - p_i^S) + \frac{1}{2} P \sum_j \sum_k y_j y_k (\delta_{ji} - \delta_{jk})}{RT} \right]$$

$$\hat{\phi}_i = \hat{\phi}_i(T, P, y_i)$$

$$\varphi_i = \varphi_i(T, P, x_i)$$

at low or moderate pressure dependence of ϕ on ψ_i may be neglected.

$$\psi_i = x_i \phi_i P_i^S / (\phi_i P)$$

$$x_i = \psi_i \phi_i P / (\psi_i P_i^S)$$

$$\therefore \sum \psi_i = 1; \sum x_i = 1$$

$$\sum x_i \psi_i P_i^S / (\phi_i P) = 1 \Rightarrow P = \sum \frac{x_i \psi_i P_i^S}{\phi_i}$$

$$\sum \psi_i \phi_i P / (\psi_i P_i^S) = 1 \Rightarrow P = \frac{\sum \psi_i \phi_i}{\sum \frac{\psi_i \phi_i}{P_i^S}}$$

using K factor

$$K_i = \frac{\psi_i}{x_i} = \frac{\psi_i P_i^S}{\phi_i P}$$

$$\therefore \sum K_i x_i = 1; \sum \frac{\psi_i}{K_i} = 1$$

Bubble pressure calculation

Given T & $\{x_i\}$ to calculate P & $\{\psi_i\}$

i) set all $\{\phi_i\} = 1.0$. Evaluate $\{P_i^S\}, \{\psi_i\}$

$$\ln P_i^S = A_i - \frac{\phi_i}{t + c_i}$$

From Van Laar Equation.

$$\ln \psi_1 = \frac{A}{(1 + \frac{A x_1}{B x_2})^2}; \ln \psi_2 = \frac{B}{(1 + \frac{B x_2}{A x_1})^2}$$

From Margules eqn.

$$\log \psi_1 = (2B - A) x_2^2 + 2(A - B) x_2^3$$

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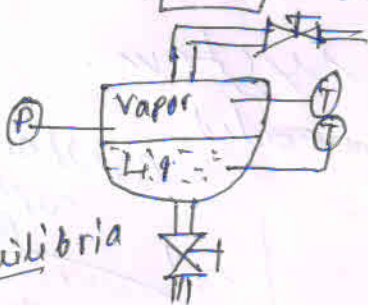
✓ Phase Equilibria

①

At equilibrium there are no driving forces for energy and mass transfer.

The system shows no tendency to depart from that equilibrium state.

no in flux X_i → system X_i → no out flux of energy, mass & momentum.



Phase equilibria

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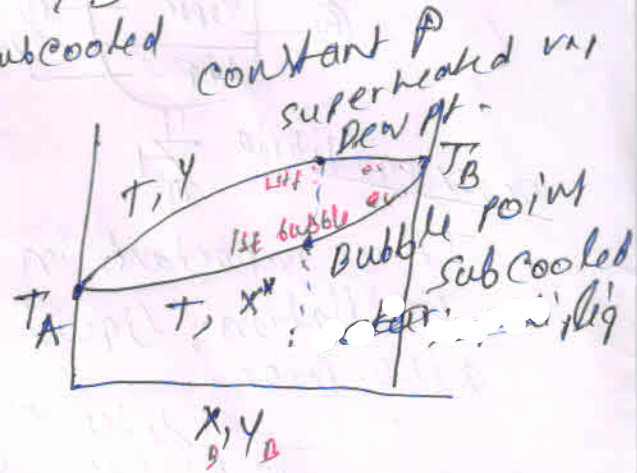
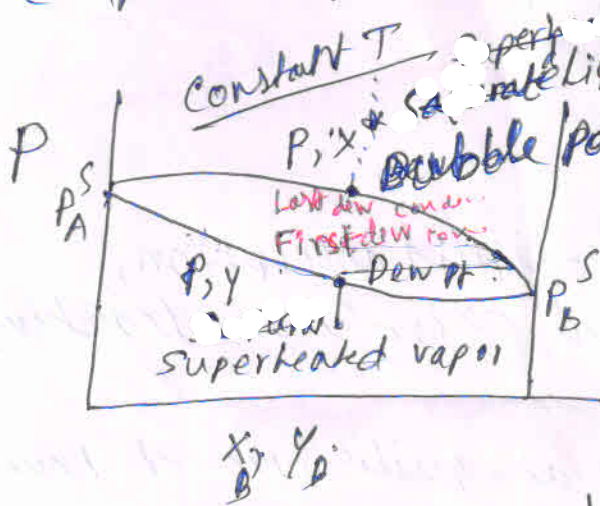
2

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Bubble pressure	specified	$T \& \{x_i\}$	computed	$P \& \{y_i\}$
Dew "	"	$T \& \{y_i\}$	"	$P \& \{x_i\}$
Bubble Temp.	"	$P \& \{x_i\}$	"	$T \& \{y_i\}$
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at eq $f_i^L = f_i^V$

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for ideal gas solution $\phi_i^V = 1$

Raoult's law ideal liquid solution $\phi_i^L = 1$ at low pressure $y_i P = x_i P_i^0$ $P_i^0 = P_i^S$

(3)

$$y_i = x_i \frac{P_i^S}{P}$$

$$x_i = y_i \frac{P}{P_i^S}$$

$$\therefore \sum y_i = \sum x_i \frac{P_i^S}{P}$$

$$\sum x_i = \sum y_i \frac{P}{P_i^S}$$

$$\Rightarrow \sum x_i P_i^S = P \quad \text{--- (i)}$$

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then $T_{\text{test}} > T_{\text{bubble}}$.

$T_{\text{new}} = T_{\text{test}} \left[\frac{\epsilon}{|\sum y_i - 1|} \right]$ and

return to ④

if $|\sum y_i - 1| < -\epsilon$. $T_{\text{test}} < T_{\text{bubble}}$.

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Dew temperature Given $P, \{y_i\}$ calculate T & $\{x_i\}$

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eq. $T_i^S = \frac{B_i}{A_i - \ln P - P_i}$

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Initialize dew temp. $T_{d,i} = \sum_i^N x_i T_i^S$

c) using computed T cal calculate $\{P_i^S\}$ & $\{\ln P_i^S = A_i - \frac{B_i}{T+C_i}\}$

d) use $x_i = \frac{P y_i}{P_i^S}$ to calculate $\{x_i\}$

e) if $|\sum x_i - 1| < \epsilon$ then $T_{\text{test}} = T_{d,i}$

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* Nonideal behaviour for both gas & liquid phases.

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$$\hat{f}_i^V = f_i^L; \quad \hat{f}_i^V = y_i \hat{\phi}_i P; \quad \hat{f}_i^L = x_i \varphi_i f_i$$

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For liquid phase (fugacity function)

$$f_i(T, P) = \phi_i^{\text{sat}} p_i^{\text{sat}} \exp \left[\frac{v_i^L (P - p_i^{\text{sat}})}{RT} \right]$$

at low P: $f_i = \phi_i^{\text{sat}} p_i^{\text{sat}}$

$$\Rightarrow y_i \hat{\phi}_i P = x_i \varphi_i \phi_i^{\text{sat}} p_i^{\text{sat}}$$

$$\Rightarrow y_i \hat{\phi}_i P = x_i \varphi_i p_i^{\text{sat}} \quad \phi_i = \frac{\hat{\phi}_i}{\phi_i^{\text{sat}}}$$

$$\hat{\phi}_i = \left(\frac{\hat{\phi}_i}{\phi_i^{\text{sat}}} \right) \exp \left[- \frac{v_i^L (P - p_i^{\text{sat}})}{RT} \right]$$

at low pressure, $P = p_i^{\text{sat}}$. $\hat{\phi}_i \approx 1 \cdot \frac{\hat{\phi}_i}{\phi_i^{\text{sat}}}$

$$\phi_i^{\text{sat}} = \exp \left[\frac{B_{ii} p_i^{\text{sat}}}{RT} \right]$$

$$\ln \hat{\phi}_i = \frac{P}{RT} (B_{ii} + Y_j^2 \delta_{ij})$$

$$\hat{\phi}_i = \exp \left[\frac{B_{ii} (P - p_i^{\text{sat}}) + \frac{1}{2} P \sum_j \sum_k Y_j Y_k (\delta_{ji} - \delta_{jk})}{RT} \right]$$

$$\hat{\phi}_i = \hat{\phi}_i(T, P, Y_i)$$

$$\varphi_i = \varphi_i(T, P, X_i)$$

at low or moderate pressure dependence of ϕ on ψ_i may be neglected.

$$\psi_i = x_i \phi_i P_i^S / (\phi_i P)$$

$$x_i = \psi_i \phi_i P / (\psi_i P_i^S)$$

$$\therefore \sum \psi_i = 1; \sum x_i = 1$$

$$\sum x_i \psi_i P_i^S / (\phi_i P) = 1 \Rightarrow P = \frac{\sum x_i \psi_i P_i^S}{\phi_i}$$

$$\sum \psi_i \phi_i P / (\psi_i P_i^S) = 1 \Rightarrow P = \frac{\sum \psi_i \phi_i}{\sum \frac{\psi_i \phi_i}{P_i^S}}$$

Using K factor

$$K_i = \frac{\psi_i}{x_i} = \frac{\psi_i P_i^S}{\phi_i P}$$

$$\therefore \sum K_i x_i = 1; \sum \frac{\psi_i}{K_i} = 1$$

Bubble pressure calculation

Given T & $\{x_i\}$ to calculate P & $\{\psi_i\}$

i) set all $\{\phi_i\} = 1.0$. Evaluate $\{P_i^S\}, \{\psi_i\}$

$$\ln P_i^S = A_i - \frac{B_i}{t + C_i}$$

From Van Laar Equation.

$$\ln \psi_1 = \frac{A}{\left(1 + \frac{A x_1}{B x_2}\right)^2}; \ln \psi_2 = \frac{B}{\left(1 + \frac{B x_2}{A x_1}\right)^2}$$

From Margules eqn.

$$\log \psi_1 = (2B - A) x_2^2 + 2(A - B) x_2^3$$

$$\log \psi_2 = (2A - B) x_1^2 + 2(B - A) x_1^3$$

- ii) Calculate $\{\phi_i\}$ from $y_i = x_i \phi_i P_i^S / (\phi_i P)$.
- iii) Evaluate $\{\phi_i\}$, from
$$\phi_i = \exp \left[\frac{B_{ii} (P - P_i^S) + \frac{1}{2} P \sum_j \sum_k y_j y_k (B_{ij} - B_{jk})}{RT} \right]$$
- iv) Calculate new form $P = \sum x_i \phi_i P_i^S / \phi_i$
- v) is $\Delta P < \epsilon$ $\Delta P = |P_{\phi_i=1} - P_{\phi_i < 1}|$ from eq. = 1.
- vi) if no, go to step ii)
- vii) if yes, end at last P_i & y_i

Dew point pressure calculation

Given T & $\{y_i\}$, to calculate P & $\{x_i\}$

i) set $\{\phi_i\} = 1$, & $\{y_i\} = 1$.

* Evaluate $\{P_i^S\}$

* Calculate P from $P = \frac{1}{\sum \frac{y_i \phi_i}{\phi_i P_i^S}}$

* Evaluate $\{x_i\}$ from

$$x_i = y_i \phi_i P / (\phi_i P_i^S)$$

* Evaluate $\{y_i\}$

using appropriate

activity coefficient model for liquid-phase.

* revise $\{\phi_i\}$ using given $\{y_i\}$ and last P .

* recalculate P using $P = \frac{1}{\sum \frac{y_i \phi_i}{\phi_i P_i^S}}$

ii) calculate @ new $\{x_i\}$ $x_i = \frac{y_i \phi_i p}{\phi_i p_i s}$

iii) calculate $\{\phi_i\}$.

iv) calculate p by $p = \frac{1}{\sum \frac{y_i \phi_i}{\phi_i p_i s}}$

v) Is $\Delta p < \epsilon \cdot (P_{new} - P_{old}) = \epsilon$.

vi) If no repeat \textcircled{i} i .

If yes. take $P \left\{ y_i \right\}$

Van-Laar Equation

$$\ln \varphi_1 = \frac{A}{\left(1 + \frac{A x_1}{B x_2}\right)^2}; \quad \ln \varphi_2 = \frac{B}{\left(1 + \frac{B x_2}{A x_1}\right)^2}$$

$$G_D^E = \frac{RTABx_1x_2}{Ax_1 + Bx_2}$$

Margules Equations

$$\ln \varphi_1 = (2B - A)x_2^2 + 2(A - B)x_2^3$$

$$\ln \varphi_2 = (2A - B)x_1^2 + 2(B - A)x_1^3$$

these can be extended to for ternary mixture.

Miscible Systems

Isopropyl alcohol ⁱⁿ ether - Isopropyl alcohol.
polar polar.

n propyl alcohol ⁱⁿ water.

Acetone ⁱⁿ chloroform

chloroform in Alcohol.

non polar x - non-polar.

n-hexane + Benzene (azeotrope)

n-hexane + cyclohexane

Benzene + " (azeotrope)

toluene + methylcyclohexane (azeotrope)

Wilson equation

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1)$$

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

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

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(-\frac{\Lambda_{12} - \Lambda_{11}}{RT}\right)$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(-\frac{\Lambda_{21} - \Lambda_{22}}{RT}\right)$$

V_1 & V_2 are pure component molar volumes.

disadvantage: It is not applicable where the logarithm of λ vs x exhibit maxima or minima.

used for completely miscible systems or limited regions of partially miscible system.

Alcohols; Alcohols & phenols.
alcohols, ketones, ethers, C₄-C₁₈ hydrocarbons.
Best fit.

NRTL equations: non-random two liquid,
partially miscible as well as completely
miscible, water or aqueous organics

nitroethane / isooctane

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right]$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT}; \quad \tau_{21} = \frac{g_{21} - g_{11}}{RT}$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}); \quad G_{21} = \exp(-\alpha_{12} \tau_{21})$$

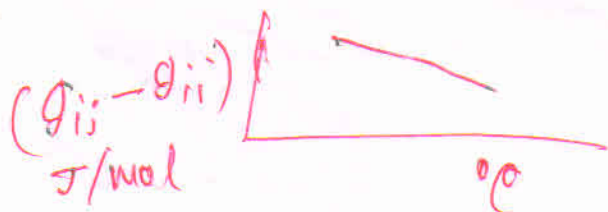
g_{ij} = energy parameter characteristic
of $i-j$ interaction; α_{12} is related

to non-randomness in mixture.

$\alpha_{12} = 0$: ~~completely~~ completely random mixture.
(0.2 - 0.47).

$$\ln \varphi_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right) + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \varphi_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right) + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$



nitroethane / isooctane

* It calculate the liq-liq equilibria

UNIQUAC (Universal quasi-chemical theory)

non-random mixtures to solutions containing molecules of different size.

$G = H - TS$

↓
Combinatorial part + residual part
↓
dominant entropic contribution. ↓
intermolecular forces → enthalpy of mixing.

Some structural parameters are

r q q' dimensionless.

$r = 3.33$ $q = 2.82$ $q' = 0.96$ CH_3OH

↓
depends on
molecular size
& surface area.

It is applicable to wide variety of non-electrolyte liquid mixture containing non polar or polar fluids → hydrocarbons, alcohols, nitriles, ketones.

Vapor liquid equilibrium for non-ideal solution

$$y_i = x_i \varphi_i P_i^s / \phi_i P \Rightarrow$$

$$\sum x_i \varphi_i P_i^s / \phi_i P = 1 \Rightarrow P = \sum \frac{x_i \varphi_i P_i^s}{\phi_i}$$

$$x_i = \frac{y_i \phi_i P}{\varphi_i P_i^s} \Rightarrow$$

$$\sum \frac{y_i \phi_i P}{\varphi_i P_i^s} = 1 \Rightarrow$$

$$P = \frac{1}{\sum \frac{y_i \phi_i}{\varphi_i P_i^s}}$$

if K factor is given

$$K_i = \frac{y_i}{x_i} = \frac{\varphi_i P_i^s}{\phi_i P}$$

$$\Rightarrow y_i = K_i x_i \Rightarrow \sum K_i x_i = 1$$

$$\Rightarrow x_i = \frac{y_i}{K_i} \Rightarrow \sum \frac{y_i}{K_i} = 1$$

Bubble pressure

given T & $\{x_i\}$, to calculate P & $\{y_i\}$

a) start with given T & $\{x_i\}$, Antoine constants, φ value for convergence.

b) set all $\{\phi_i\} = 1$, evaluate P_i^s from Antoine eq' & $\{\varphi_i\}$ from NRTL, Wilson, etc.

calculate
$$P = \sum \frac{x_i \varphi_i P_i^s}{\phi_i}$$

c) calculate $\{y_i\}$ from $y_i = \frac{x_i \varphi_i P_i^s}{\phi_i P}$

d) calculate $\{\phi_i\}$ from $\phi_i = \exp \frac{B_{ii}(P - P_i^s) + \frac{1}{2} P \sum_{j \neq i} y_j V_{ij} K_{ij}}{RT}$ ($\delta_{ij} = \frac{V_{ij}}{V_i}$)

e) calculate P_{new} from $P = \sum \frac{x_i \varphi_i P_i^s}{\phi_i}$

A) if $\delta P < \epsilon$ end at last P and $\{y_i\}$.

B) if $\delta P > \epsilon$ go to step c) and calculate new $\{y_i\}$ with last $\{\phi_i\}$.

Dew point pressure

(2)

Given T & $\{y_i\}$, to calculate P & $\{x_i\}$

a) Start with T , $\{y_i\}$, Antoine constant and δ (error value).

1) set $\{\phi_i\} = 1$, $\{\psi_i\} = 1$; evaluate $\{P_i^s\}$

calculate P using
$$P = \frac{1}{\sum \frac{y_i \phi_i}{\psi_i P_i^s}}$$

Evaluate $\{\psi_i\}$ from appropriate model.

Recalculate P .

b) calculate $\{\phi_i\}$ using given $\{y_i\}$ and last P .

c) calculate $\{x_i\}$
$$x_i = \frac{y_i \phi_i P}{\psi_i P_i^s}$$

d) Normalize $\{x_i\}$ using $x_{in} = \frac{x_i}{\sum x_i}$

and use normalized $\{x_i\}$ to calculate $\{\psi_i\}$

e) Recalculate
$$P = \frac{1}{\sum \frac{y_i \phi_i}{\psi_i P_i^s}}$$

f) IF $\Delta P < \epsilon$. end with last P & $\{x_i\}$

g) IF $\Delta P > \epsilon$. go to Step b)

Bubble Temperature

(3)

Given P & $\{x_i\}$ to calculate T and $\{y_i\}$

a) Solve for T and $\{y_i\}$ by assuming Raoult's law algorithm for bubble T

b) Estimate $\{k_i\}$ from $k_i = \frac{y_i}{x_i}$

c) calculate $y_i = \frac{k_i x_i}{\sum k_i x_i}$ [normalized]

d) using normalized $\{y_i\}$ calculate $\{k_i\}$ and $\sum k_i x_i$

e) if $\sum k_i x_i = 1$ end with last T & $\{y_i\}$

f) if $\sum k_i x_i > 1$, then $T_{\text{last}} > T_b$

$T_{\text{new}} = T_{\text{last}} \frac{1}{\sum k_i x_i}$ and return to step c) and return to step b).

g) if $\sum k_i x_i < 1$ then $T_{\text{last}} < T_b$

$T_{\text{new}} = T_{\text{last}} \sum k_i x_i$
and return to step c) and return to step b).

Dew temperature

Given P and $\{y_i\}$ to calculate T & $\{x_i\}$

- a) Solve for T and $\{x_i\}$ by assuming Raoult's law algorithm for dew point T .
 - b) calculate $k_i = \frac{y_i}{x_i}$.
 - c) calculate $x_i = \frac{y_i/k_i}{\sum (y_i/k_i)}$ [normalized]
 - d) using normalized $\{x_i\}$, calculate $\{k_i\}$ and $\sum y_i/k_i$
 - e) if $\sum y_i/k_i = 1$ end with last T & $\{x_i\}$
 - f) if $\sum y_i/k_i > 1$ $T_{last} < T_d$
 $T_{new} = T_{last} \sum \frac{y_i}{k_i}$
and return to step b)
 - g) if $\sum y_i/k_i < 1$ $T_{last} > T_d$
 $T_{new} = T_{last} \sum \frac{y_i}{k_i}$
and return to step b)
-

Vapor-Liquid equilibrium for non ideal mixture

1. Estimate the activity coefficients for a methanol (1), ethanol (2), isopropyl alcohol (IPA) (3), and water (4) liquid mixture with $x_1 = 0.05$, $x_2 = 0.05$, $x_3 = 0.18$ and $x_4 = 0.72$, respectively. Wilson equation is given as,

$$\ln \gamma_k = 1.0 - \ln \left[\sum_{j=1}^n (x_j A_{kj}) \right] - \sum_{i=1}^n \left[\frac{x_i A_{ik}}{\sum_{j=1}^n (x_j A_{ij})} \right]$$

The values of binary pair A_{ij} is given by

		j			
		1	2	3	4
i	1	1	2.3357	2.7385	0.4180
	2	0.1924	1	1.6500	0.1108
	3	0.2419	0.5343	1	0.0465
	4	0.9699	0.9560	0.7795	1

2. Estimate the bubble point temperature and vapor composition for the liquid mixture with given composition at a total pressure of 101.3 kPa with a **Matlab** code. Use the Wilson model with the parameters:

$$\ln P_{sat}^1 (\text{kPa}) = 16.58 - \frac{3638.37}{T(^{\circ}\text{C}) + 239.50}$$

$$\ln P_{sat}^2 (\text{kPa}) = 16.90 - \frac{3795.17}{T(^{\circ}\text{C}) + 230.91}$$

$$\ln P_{sat}^3 (\text{kPa}) = 16.68 - \frac{3640.20}{T(^{\circ}\text{C}) + 219.61}$$

$$\ln P_{sat}^4 (\text{kPa}) = 16.39 - \frac{3885.70}{T(^{\circ}\text{C}) + 230.17}$$

Bubble point calculation

1. Calculate saturation temperature for all component from Antoine equation for the given pressure.

$$T_s(i) = \frac{B(i)}{A(i) - \ln(P)} - C(i)$$

2. Initialize bubble temperature $T_i = \sum_1^n x(i)T_s(i)$
3. Solve the equation for bubble temperature T_b with the initial guess,

$$P - \sum_{i=1}^n \gamma(i)x(i)\exp\left[A(i) - \frac{B(i)}{C(i) + T}\right] = 0$$

4. Calculate $\ln P_{sat}^i$ (kPa) from Antoine equation with the new value of T_b ;

$$\text{Calculate } y(i) = \frac{\gamma(i)x(i)P_{sat}^i}{P}$$

5. If $\text{abs}(T_b - T_i) < \text{eps}$; $T = T_b$
6. Else $T_i = T_b$ go to step 3.

APPENDIX B

NRTL PARAMETERS AND ANTOINE COEFFICIENTS

Tables B.1, B.2, and B.3 give binary interaction parameters (a , b , and c , respectively) for the NRTL equation (Equations B.1 and B.2) for systems that have been used and discussed extensively throughout the book. All parameters are regressed values from the Dortmund databank, obtained from Aspen Plus[®].

$$\gamma_i = \exp \left[\frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \right] \quad (\text{B.1})$$

$$\text{where } \tau_{ij} = a_{ij} + b_{ij}/T(K) \quad \text{and} \quad G_{ij} = \exp(-c_{ij}\tau_{ij}) \quad (\text{B.2})$$

Example of Using Tables B.1–B.3

Suppose the binary interaction coefficients are being sought for the benzene–water system. We shall designate benzene as component i and water as component j . Then, in Table B.1, progress down the first column until component i is found (benzene). Then, progress down the row where component i has been found and search for the cell intersection with component j in the first row. It can be seen that $a_{ij} = 45.191$. To find a_{ji} , repeat the procedure, but search for component j in the first column, and then for the cell intersection with component i in the first row. In this

Understanding Distillation Using Column Profile Maps, First Edition. Daniel Beneke, Mark Peters, David Glasser, and Diane Hildebrandt.

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TABLE B.4 Antoine Equation Coefficients for Selected Components

	Methanol	Ethanol	Benzene	<i>p</i> -Xylene	Toluene	Chloroform	Water	Acetone
<i>A</i>	8.07240	8.1122	6.90565	6.99052	6.95464	6.93710	8.01767	7.23160
<i>B</i>	1574.990	1592.864	1211.033	1453.430	1344.800	1171.200	1715.7	1277.030
<i>C</i>	238.870	226.184	220.790	215.307	219.482	227.000	234.268	237.230

example, $a_{ji} = 140.087$. Using a similar procedure, values for parameters b and c can also be found.

The Antoine equation for calculating vapor pressure is given in Equation B.3, with the relevant constants in Table B.4.

$$\ln(P_i^{\text{VAP}}) = A_i - \frac{B_i}{T + C_i} \quad (\text{B.3})$$

Liquid-Liquid equilibria

A & B comprise the original binary mixture.

if A or B forms azeotrope or difference in volatility is very low.

The third solvent C is added to A+B, the solvent is partially miscible or immiscible with original mixture or solution.

→ Two liquid phase results.

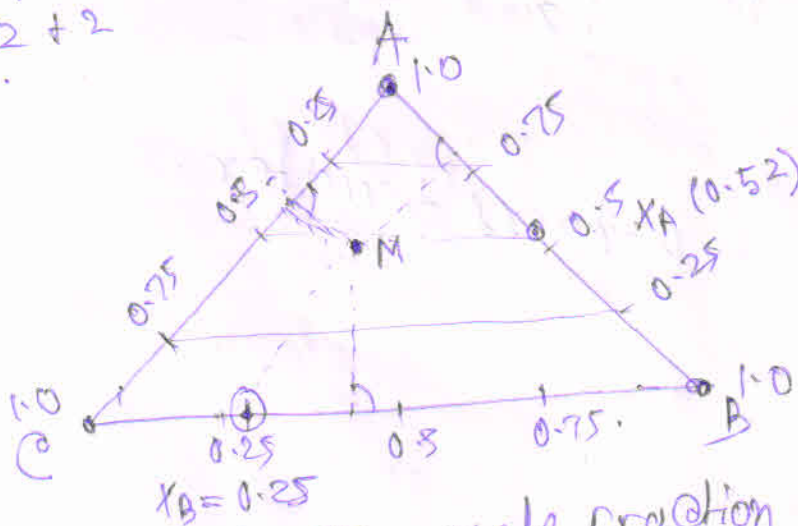
Extract phase
 Preferentially extract

Raffinate phase
 ↓
 most of the B remaining and less A exists.

$$F = C - P + 2$$

$$= 3 - 2 + 2$$

$$= 3$$



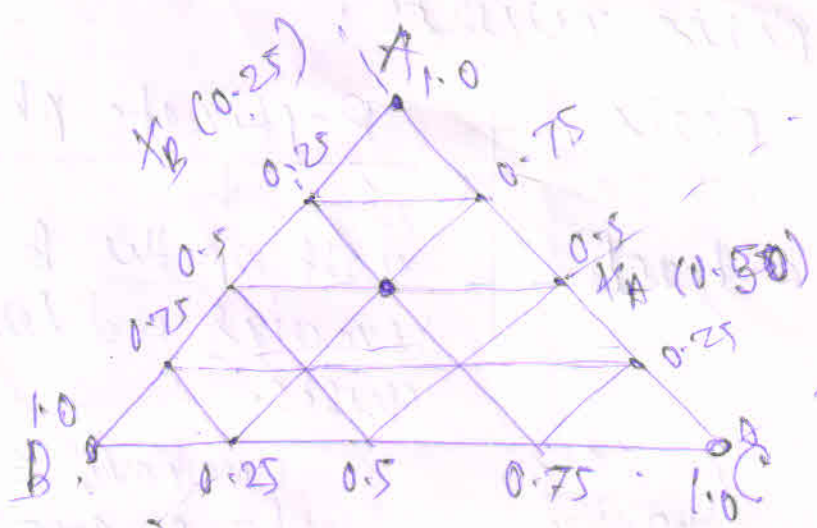
We have 6 variables.
 T, P, concentrations 4.
 T, P, & 1 concentration are specified.
 The system will be fixed by 3.
 concentrations must be calculated from phase equilibrium.

Each apex → 100% mole fraction of the species.
 Each side → a mixture of two species.

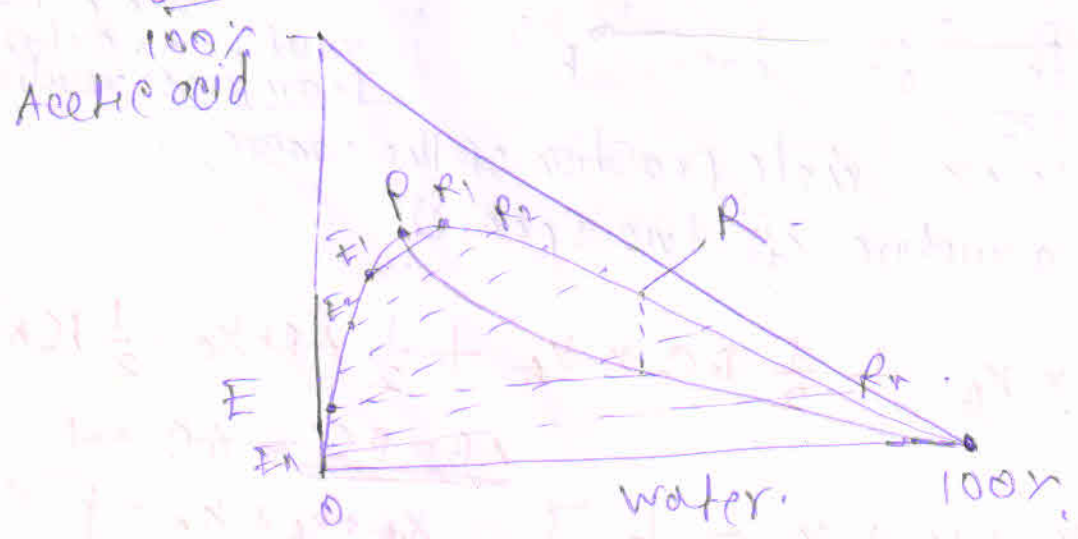
$$\frac{1}{2} AC \times X_B + \frac{1}{2} BC \times X_A + \frac{1}{2} AB \times X_C = \frac{1}{2} BC \times h$$

$$\underline{AB = BC = AC = 1}$$

$$\therefore X_B + X_A + X_C = h \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} X_A + X_B + X_C = 1$$

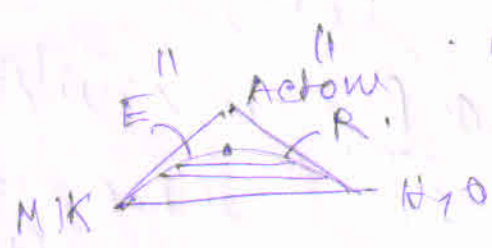


acetic acid + Benzene + water.



Type one acetone-water-methyl isobutyl ketone.

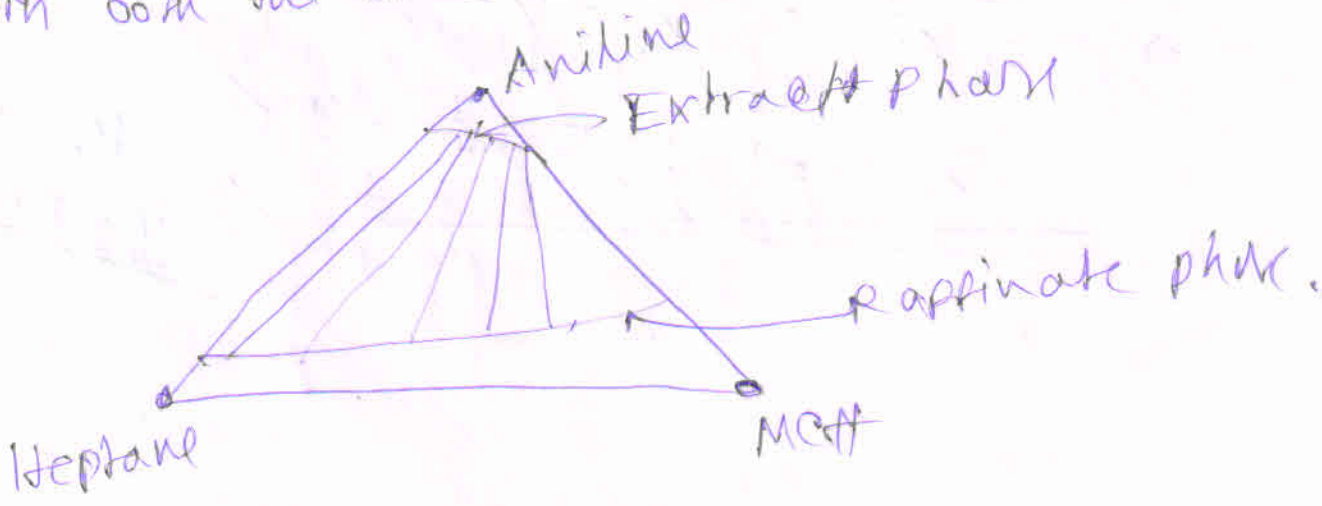
partial miscibility of solvent MIK & dilute water
 complete miscibility of acetone (component to be extracted)

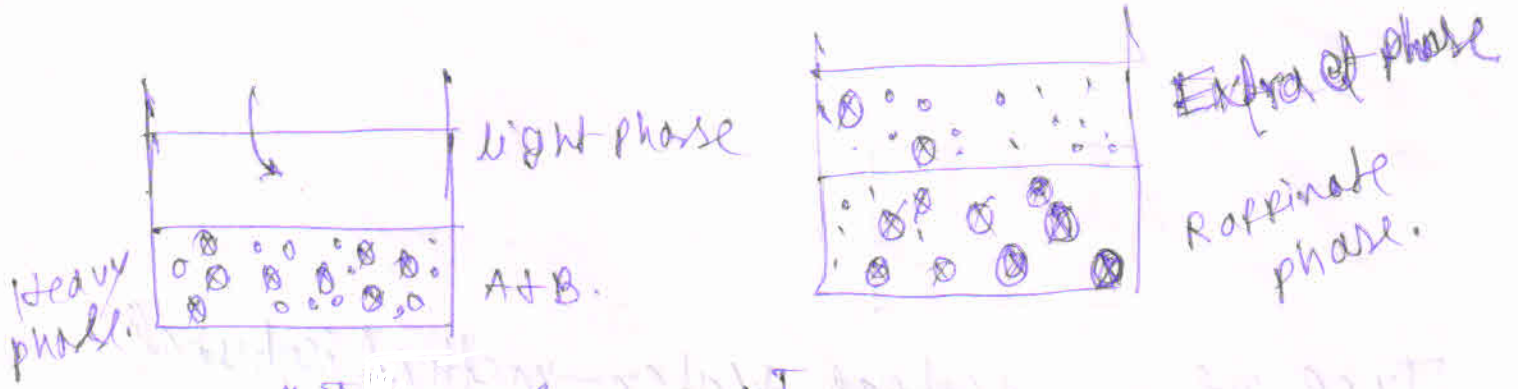


Type II

Aniline - n-heptane - methylcyclohexane (MCH)

Solvent aniline is only partially miscible with both the other components.





$$f_i^I = (x_i \varphi_i f_i^I)$$

$$f_i^{II} = (x_i \varphi_i f_i^{II})$$

at same T & P , at equilibrium.

$$f_i^I = f_i^{II} \quad (\text{pure component fugacities})$$

$$f_i^I = f_i^{II}$$

$$(x_i \varphi_i)^I = (x_i \varphi_i)^{II}$$

$$x_i^I \varphi_i^I = x_i^{II} \varphi_i^{II}$$

$$\left. \begin{aligned} \Sigma x_i^I &= 1 ; \Sigma x_i^{II} = 1 \end{aligned} \right\}$$

$$\begin{aligned} x_1^I, x_2^I \\ x_1^{II}, x_2^{II} \end{aligned}$$

$$y = f(x)$$

Liquid-Liquid equilibria

A & B comprise the original binary mixture.

if A or B forms azeotrope or difference in volatility is very low.

The third solvent C is added to A+B, the solvent is partially miscible or immiscible with original mixture or solution.

→ Two liquid phase results.

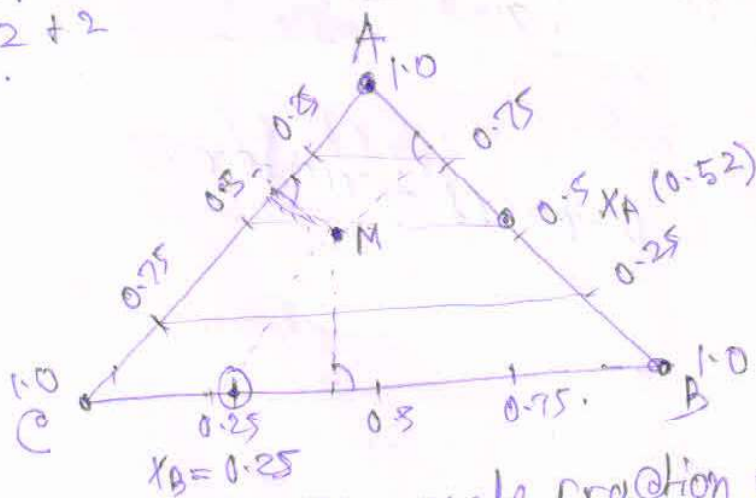
Extract phase
↓
Preferentially extract

Raffinate phase
↓
most of the B remaining and less A exists.

$$F = C - P + 2$$

$$= 3 - 2 + 2$$

$$= 3$$



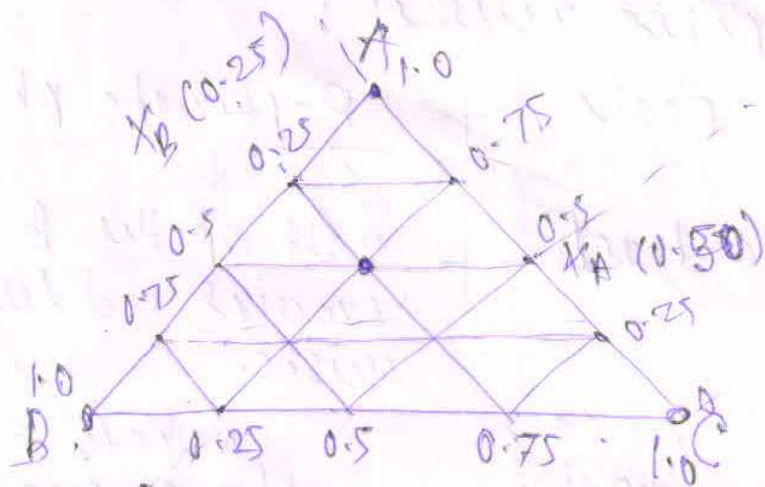
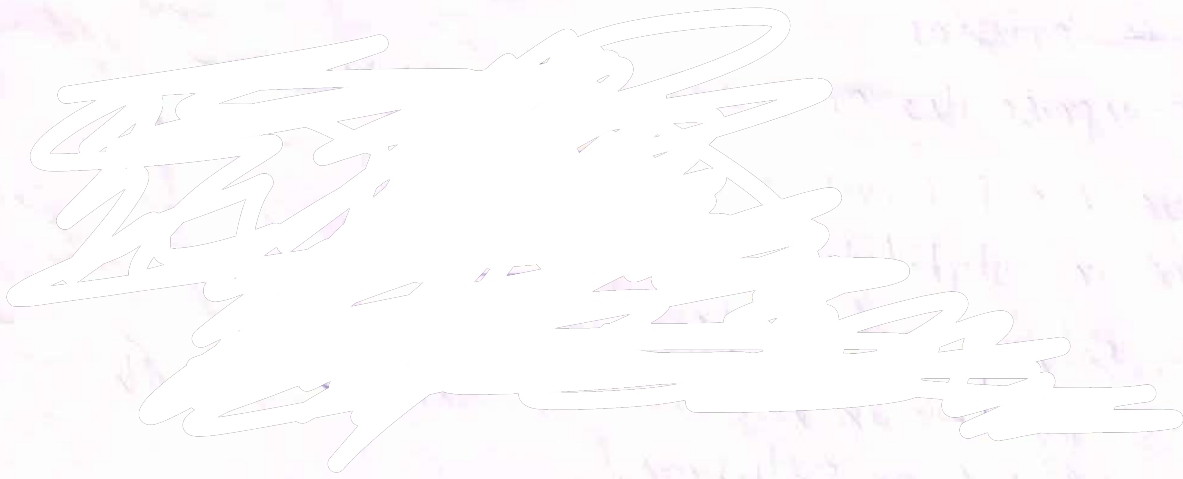
We have 6 variables.
T, P, concentrations 4.
T, P, 1 concentration are specified.
The system will be fixed by 3 concentrations.
must be calculated from phase equilibrium.

Each apex → 100% mole fraction of the species.
Each side → a mixture of two species.

$$\frac{1}{2} AC \times X_B + \frac{1}{2} BC \times X_A + \frac{1}{2} AB \times X_C = \frac{1}{2} BC \times h$$

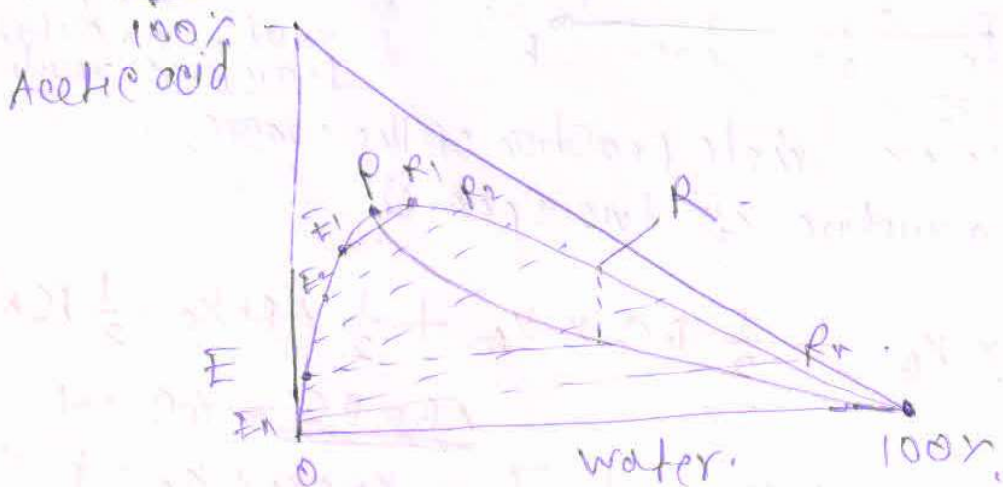
$$\underline{AB = BC = AC = h}$$

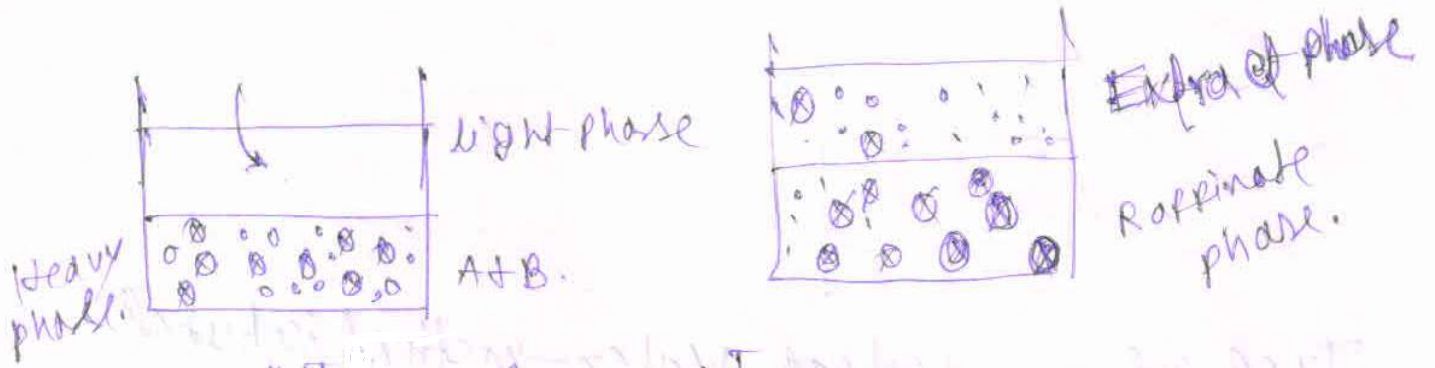
$$\therefore X_B + X_A + X_C = h \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} X_A + X_B + X_C = 1$$



$x_C (0.25)$

acetic acid + Benzene + water.





$$f_i^I = (x_i \varphi_i f_i)^I$$

$$f_i^{II} = (x_i \varphi_i f_i)^{II}$$

at same T & p , at equilibrium.

$$f_i^I = f_i^{II} \quad (\text{pure component fugacity})$$

$$f_i^I = f_i^{II}$$

$$\therefore (x_i \varphi_i)^I = (x_i \varphi_i)^{II}$$

$$\Rightarrow x_i^I \varphi_i^I = x_i^{II} \varphi_i^{II}$$

$$\left. \begin{aligned} \Sigma x_i^I &= 1 & \Sigma x_i^{II} &= 1 \end{aligned} \right\}$$

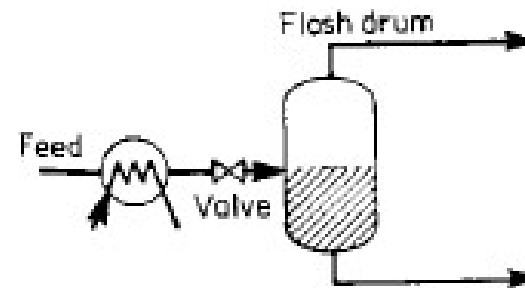
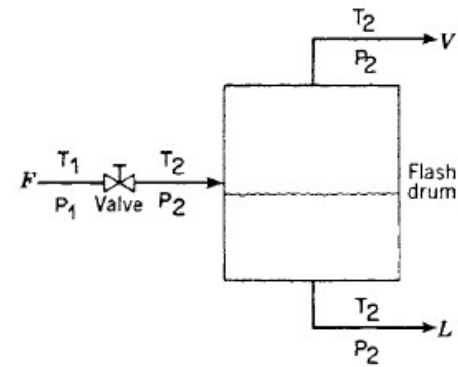
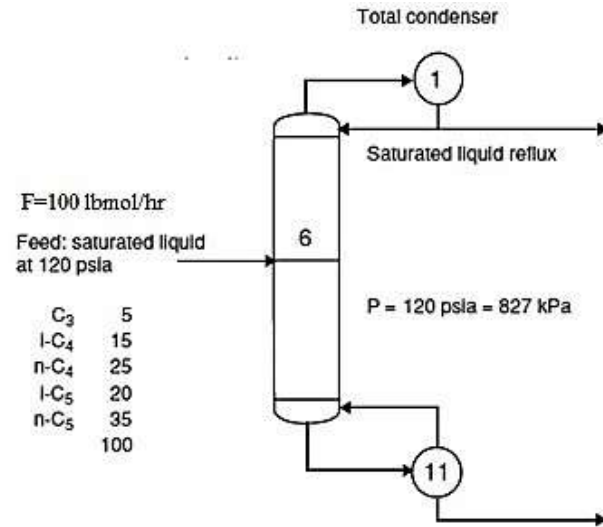
$$\begin{aligned} x_1^I, x_2^I \\ x_1^{II}, x_2^{II} \end{aligned}$$

$$\varphi = f(\varphi)$$

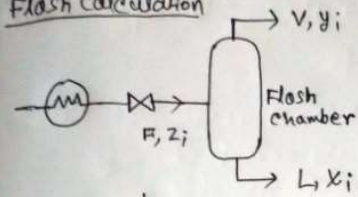
Flash Calculation

Rachford-Rice Equation

Distillation and Flash Operations



Flash Calculation



at steady state

Overall material balance

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

composition balance

$$F z_i = V y_i + L x_i \quad \text{--- (ii)}$$

put $y_i = K_i x_i$ --- (iii)

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

Putting $L = F - V$

$$F z_i = K_i x_i V + (F - V) x_i$$

$$\Rightarrow x_i = \frac{z_i}{1 + (V/F)(K_i - 1)} \quad \text{--- (iv)}$$

Putting $x_i = \frac{y_i}{K_i}$ in (ii) and $L = F - V$

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

$$\Rightarrow y_i = \frac{K_i z_i}{1 + (V/F)(K_i - 1)} \quad \text{--- (v)}$$

Now $\sum y_i - \sum x_i = 0$

$$\sum \frac{K_i z_i}{1 + (V/F)(K_i - 1)} - \sum \frac{z_i}{1 + (V/F)(K_i - 1)} = 0$$

equilibrium relations:

$$y_i = K_i x_i$$

$$i = 1, 2, \dots, n$$

no species

$$\sum x_i = 1$$

$$\sum y_i = 1$$

$$\sum \frac{z_i (K_i - 1)}{1 + (V/F)(K_i - 1)} = 0$$

Rachford-Rice equation

- Estimate i) vapor split, ii) vapor and liquid phase compositions in a flash chamber using Aspen plus/Rachford–Rice equation.

$$x_i = \frac{z_i}{1 + (V/F)(K_i - 1)}$$

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

Since $\sum x_i - \sum y_i = 0$,

$$f\left(\frac{V}{F}\right) = \sum_i \frac{z_i(1 - K_i)}{1 + (V/F)(K_i - 1)} = 0 \quad \text{Rachford–Rice equation}$$

Components, i	{z _i }	Phase Equilibrium K-value
propane	0.1	6.8
n-butane	0.3	2.2
n-pentene	0.4	0.8
n-octane	0.2	0.052

Text books

- Introduction to Chemical Engineering Computing, Bruce A Finlayson, JOHN WILEY & SONS, INC., PUBLICATION.

Thank You

Activity coefficient model

1. Estimate the activity coefficients for a methanol (1), ethanol (2), isopropyl alcohol (IPA) (3), and water (4) liquid mixture with $x_1 = 0.05$, $x_2 = 0.05$, $x_3 = 0.18$ and $x_4 = 0.72$, respectively. Wilson equation is given as,

$$\ln \gamma_k = 1.0 - \ln \left[\sum_{j=1}^n (x_j A_{kj}) \right] - \sum_{i=1}^n \left[\frac{x_i A_{ik}}{\sum_{j=1}^n (x_j A_{ij})} \right]$$

The values of binary pair A_{ij} is given by

		<i>j</i>			
		1	2	3	4
<i>i</i>	1	1	2.3357	2.7385	0.4180
	2	0.1924	1	1.6500	0.1108
	3	0.2419	0.5343	1	0.0465
	4	0.9699	0.9560	0.7795	1

2. Estimate the bubble point temperature and vapor composition for the liquid mixture with given composition at a total pressure of 101.3 kPa with a **Matlab** code. Use the Wilson model with the parameters:

$$\ln P_{sat}^1 (\text{kPa}) = 16.58 - \frac{3638.37}{T(^{\circ}\text{C}) + 239.50}$$

$$\ln P_{sat}^2 (\text{kPa}) = 16.90 - \frac{3795.17}{T(^{\circ}\text{C}) + 230.91}$$

$$\ln P_{sat}^3 (\text{kPa}) = 16.68 - \frac{3640.20}{T(^{\circ}\text{C}) + 219.61}$$

$$\ln P_{sat}^4 (\text{kPa}) = 16.39 - \frac{3885.70}{T(^{\circ}\text{C}) + 230.17}$$

NRTL PARAMETERS

$$\gamma_i = \exp \left[\frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \right]$$

where $\tau_{ij} = a_{ij} + b_{ij}/T(K)$ and $G_{ij} = \exp(-c_{ij}\tau_{ij})$

TABLE B.1 Binary Interaction Parameter a_{ij} for the NRTL Model for Selected Components

	Methanol	Ethanol	Benzene	<i>p</i> -Xylene	Toluene	Chloroform	Water	Acetone
Methanol	0.000	4.712	-1.709	0.678	0.000	0.000	-0.693	0.000
Ethanol	-2.313	0.000	0.569	4.075	1.146	0.000	-0.801	-1.079
Benzene	11.580	-0.916	0.000	0.000	-2.885	0.000	45.191	0.422
<i>p</i> -Xylene	-3.259	-5.639	0.000	0.000	0.000	0	2.773	0.000
Toluene	0.000	-1.722	2.191	0.000	0.000	0.000	-247.879	-1.285
Chloroform	0.000	0.000	0.000	0	0.000	0.000	-7.352	0.538
Water	2.732	3.458	140.087	162.477	627.053	8.844	0.000	0.054
Acetone	0.000	-0.347	-0.102	0.000	1.203	0.965	6.398	0.000

Bubble point calculation

1. Calculate saturation temperature for all component from Antoine equation for the given pressure.

$$T_s(i) = \frac{B(i)}{A(i) - \ln(P)} - C(i)$$

2. Initialize bubble temperature $T_i = \sum_1^n x(i)T_s(i)$
3. Solve the equation for bubble temperature T_b with the initial guess, assuming vapor-phase ideal, i.e., fugacity coefficient $\varphi=1$.

$$P - \sum_{i=1}^n \gamma(i)x(i)\exp\left[A(i) - \frac{B(i)}{C(i) + T}\right] = 0$$

4. Calculate $\ln P_{sat}^i$ (kPa) from Antoine equation with the new value of T_b ;

$$\text{Calculate } y(i) = \frac{\gamma(i)x(i)P_{sat}^i}{P}$$

5. If $abs(T_b - T_i) < \text{eps}$; $T=T_b$
6. Else $T_i = T_b$ go to step 3.

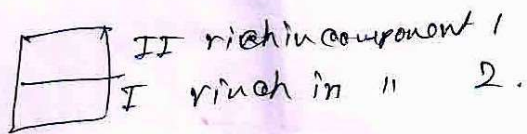
Liquid-Liquid equilibrium and phase distributions computation

Example

Use the Van-Laar activity coefficient expression to predict the compositions of co-existing liquid phases (I & II) comprised of two partially miscible liquids (1) & (2) at 50°C and 4 bar

$$\ln \phi_1 = \frac{A_{12}}{\left[1 + \frac{A_{12}x_1}{A_{21}x_2}\right]^2}; \quad \ln \phi_2 = \frac{A_{21}}{\left[1 + \frac{A_{21}x_2}{A_{12}x_1}\right]^2}$$

$$A_{12} = 2.5, \quad A_{21} = 3.5$$



$$P = C - F + 2 \\ = 2 - 2 + 2 \\ = 2$$

For component 1

$$x_1^I \phi_1^I = x_1^{II} \phi_1^{II}$$

$$x_1^I \exp\left(\frac{A_{12}}{\left[1 + \frac{A_{12}x_1^I}{A_{21}x_2^I}\right]^2}\right) = x_1^{II} \exp\left(\frac{A_{21}}{\left[1 + \frac{A_{21}x_2^{II}}{A_{12}x_1^{II}}\right]^2}\right)$$

For component 2:

$$x_2^I \exp\left(\frac{A_{21}}{\left[1 + \frac{A_{21}x_2^I}{A_{12}x_1^I}\right]^2}\right) = x_2^{II} \exp\left(\frac{A_{12}}{\left[1 + \frac{A_{12}x_1^{II}}{A_{21}x_2^{II}}\right]^2}\right)$$

$$x_1^I + x_2^I = 1$$

$$x_1^{II} + x_2^{II} = 1$$

$$\left. \begin{array}{l} y_1^I = 0.12, \quad x_2^{II} = 0.88 \\ x_1^{II} = 0.25, \quad x_2^I = 0.15 \end{array} \right\}$$