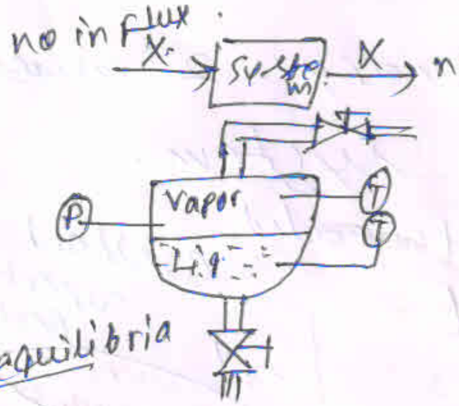
Phase Equilibria

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

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



no out flux 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

$\mu_i^\alpha = \mu_i^\beta$ α & β are two phases

$G^\alpha = G^\beta$ molar Gibbs free energy.

$\Rightarrow dG^\alpha = dG^\beta$. $V^\alpha dP^{sat} - S^\alpha dT = V^\beta dP^{sat} - S^\beta dT$

$$\Rightarrow \frac{dP^{sat}}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S}{dV}$$

$dS = \frac{dQ}{T}$; $dQ = dH$ at contant P.

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T \Delta V^{\alpha\beta}}$$ Clapeyron eq.

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

Antonie eqn

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

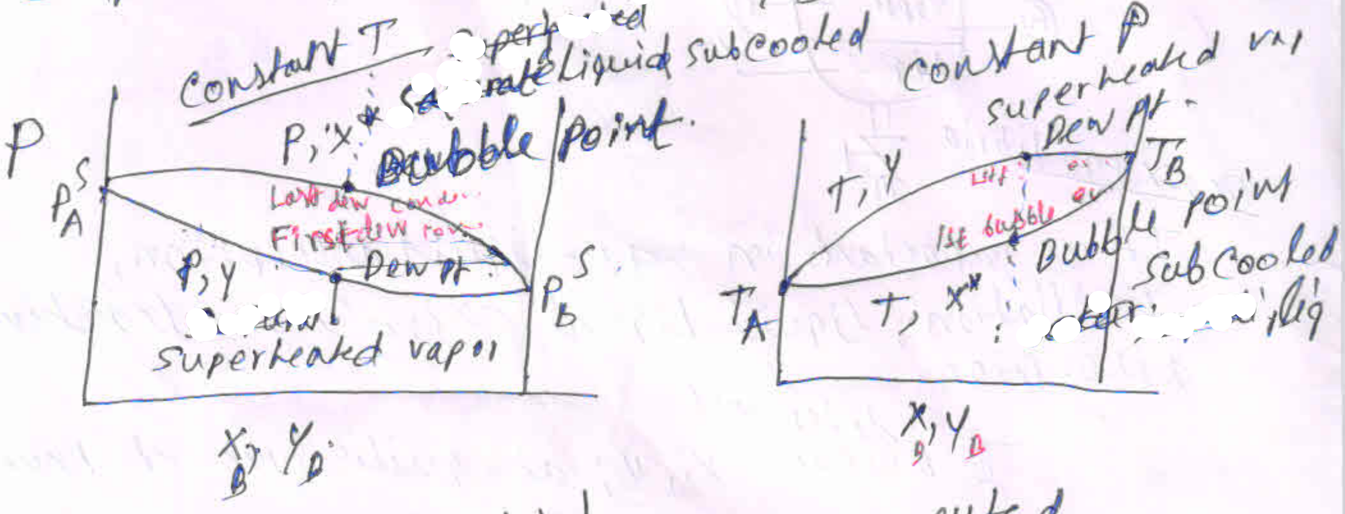
$$\frac{dP^{sat}/P^{sat}}{dT/T^2} = \frac{\Delta H^{\alpha\beta}}{R}.$$

degree of freedom

$F = C - P + 2$

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

$F = 2 - 2 + 2 = 2$, specify 2 variables for complete explanation of system.



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

at eq $f_i^l = f_i^V$.

$$f_i^l = x_i \varphi_i^l f_i^0$$

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

for ideal gas solution $\bar{\varphi}_i^v = 1$;

$$y_i \bar{\phi}_i^V P = x_i \varphi_i^l f_i^0$$

---

ideal liquid solution $\varphi_i^l = 1$

at low pressure

Raoult's law $y_i P = x_i P_i^S$ $\quad$ $f_i^0 = P_i^S$

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

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

$\Rightarrow \sum x_i P_i^S = P$ —(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 & $\{y_i\}$ given T & $\{x_i\}$

Calculate P using $\sum x_i P_i^S = P$.
calculate P_i^S " Anotnie eqn..
calculat $\{y_i\}$ " $y_i = x_i \frac{P_i^S}{P}$.

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 " Antonie eqn.

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

Bubble Temp calculation

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

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 $\{y_i\}$

e) if $|\sum y_i - 1| < \varepsilon$. $T_{test} = T_{bubble}$.

f) if $\sum y_i - 1 > \varepsilon$.

then T $T_{test} > T_{b(P)}$.

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

return to c)

if $\sum y_i - 1 < -\varepsilon$. $T_{test} < T_{b(P)}$.

$$T_{new} = T_{test}\frac{|\sum y_i - 1|}{\varepsilon}$$ & return to step c)

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

a) compute T_i^S for a give pressure. From Anotonie eq.. $T_i^S = \frac{B_i}{A_i - \ln P} - C_i$

b)

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 $|\sum x_i - 1| < \varepsilon$ Then $T_{test} = T_{d,i}$

f) If $\sum x_i - 1 > \varepsilon$ then $T_{test} < T_{d,i}$; $T_{new} = \frac{\sum x_i - 1}{\varepsilon}$

and return to step b).

g) If $\sum x_i - 1 < -\varepsilon$ then $T_{test} > T_{d,i}$; $T_{new} = \frac{|\sum x_i - 1|}{\varepsilon}$

& 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.

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

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

For liquid phase (fugacity function)

$$f_i(T,P) = \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^l (P - P_i^{sat})}{RT}\right]$$

at low P. $f_i = \phi_i^{sat} P_i^s$.

$$\Rightarrow y_i \hat{\phi}_i P = x_i \varphi_i \phi_i^s P_i^s$$

$$\Rightarrow y_i \phi_i P = x_i \varphi_i P_i^s \qquad \phi_i = \frac{\hat{\phi}_i}{\phi_i^s}.$$

$$\phi_i = \left(\frac{\hat{\phi}_i}{\phi_i^s}\right) \exp\left[-\frac{V_i^l (P - P_{sat})}{RT}\right]$$

at low pressure, $P = P_{sat}$. $\phi_i \approx \frac{\hat{\phi}_i}{\phi_i^s}$

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

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

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

$$\phi_i = \phi_i(T, P, y_i).$$

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

at low or moderate pressure dependence of Φ P on γ_i may be neglected.

$$y_i = x_i \gamma_i P_i^s / (\Phi_i P).$$

$$x_i = y_i \Phi_i P / (\gamma_i P_i^s).$$

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

$$\sum x_i \gamma_i P_i^s / (\Phi_i P) = 1 \Rightarrow P = \sum \frac{x_i \gamma_i P_i^s}{\Phi_i}$$

$$\sum y_i \Phi_i P / (\gamma_i P_i^s) = 1 \Rightarrow P = \frac{1}{\sum \frac{y_i \Phi_i}{\gamma_i P_i^s}}.$$

using K factor

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^s}{\Phi_i P}.$$

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

Bubble pressure calculation

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

i) set all $\{\Phi_i\} = 1.0$. Evaluate $\{P_i^s\}$, $\{\gamma_i\}$

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

From van Laar Equation.

$$\ln \gamma_1 = \frac{A}{\left(1 + \frac{A x_1}{B x_2}\right)^2} ; \ln \gamma_2 = \frac{B}{\left(1 + \frac{B x_2}{A x_1}\right)^2}$$

From Margules eq^n.

$$\log \gamma_1 = (2B - A) x_2^2 + 2(A - B) x_2^3$$

$$\log \gamma_2 = (2A - B) x_1^2 + 2(B - A) x_1^3$$

ii) calculat$\{y_i\}$ form $y_i = x_i \gamma_i P_i^S/(\phi_i P)$.

iii) Evaluate $\{\phi_i\}$, from

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

iv) calculate Pnew fom $P = \sum x_i \gamma_i P_i^S/\phi_i$

v) is $\Delta P < \varepsilon$ $\Delta P = |P_{\phi_i=1} - P_{\phi_i<1}|$ from el $=1$.

vi) if no, go to step ii)

vii) if yes, end at last P, & y_i

Dew point pressure calculation

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

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

*Evaluate $\{P_i^S\}$

* calculate P from $P = \dfrac{1}{\sum \frac{y_i\phi_i}{\gamma_i P_i^S}}$.

*evaluate $\{x_i\}$ from

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

*Evaluate $\{\gamma_i\}$ using appropriate activity co-efficient model for Liquid-phase.

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

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

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

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

iv) calculate P by. $P = \frac{1}{\sum \frac{y_i \phi_i}{\varphi_i P_i^s}}$

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

vi) If no repeat. ⓘ. i.
If yes. take P & $\{y_i\}$

Van-Laar Equation

$$\ln \gamma_1 = \frac{A}{\left(1 + \frac{A x_1}{B x_2}\right)^2} ; \quad \ln \gamma_2 = \frac{B}{\left(1 + \frac{B x_2}{A x_1}\right)^2}$$

$$G_{B}^{E} = \frac{RTAB x_1 x_2}{A x_1 + B x_2}$$

Margules Equations

$$\ln \gamma_1 = (2B - A) x_2^2 + 2(A - B) x_2^3 .$$

$$\ln \gamma_2 = (2A - B) x_1^2 + 2(B - A) x_1^3 .$$

these can be extended ~~to~~ for Ternary mixture.

miscible Systems

Isopropyl ~~ate~~ ether in Isopropyl alcohol.
polar polar.

n propyl alchohol in water.

Acetone in chloroform

chloroform in Alcohol.

non polar – non-polar.

n-hexane + Benzene (azeotrope

n- " + cyclohexane

Benene + " (azeotrope)

toluene + methylcyclo hexane (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 logarithms 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, $C_4 - C_{18}$ hydrocarbons.

Best fit.

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

nitroethane / isooctane

$$\frac{g^E}{RT} = x_1x_2\left[\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right]$$

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

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

g_{ij} = energy parameter characteristic of i-j interaction, α_{12} is related to non-randomness in mixture.

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

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right]$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right]$$

✗ It calculate the liq-liq equilibria

UNIQUAC (Universal quasi-chemical theory).

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

$G = H - TS$

$g^E \rightarrow$ Combinatorial part + residual part

Combinatorial part ↓ dominant entropic contribution.

residual part ↓ intermolecular forces → enthalpy of mixing.

some structural parameters are

	r	q	q'	dimensionless.
CCl_4	3.33	2.82	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.

$\overline{\text{VII}}$

Vapor liquid equilibria for non-ideal solution

$$y_i = x_i \gamma_i P_i^S / \hat{\phi}_i P \Rightarrow \boxed{\sum x_i \gamma_i P_i^S / \hat{\phi}_i P = 1} \Rightarrow \boxed{P = \sum \frac{x_i \gamma_i P_i^S}{\hat{\phi}_i}}$$

$$x_i = \frac{y_i \hat{\phi}_i P}{\gamma_i P_i^S} \Rightarrow \boxed{\sum \frac{y_i \hat{\phi}_i P}{\gamma_i P_i^S} = 1} \Rightarrow P = \frac{1}{\sum \frac{y_i \hat{\phi}_i}{\gamma_i P_i^S}}$$

if K factor is given

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^S}{\hat{\phi}_i P}$$

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

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

Bubble pressure

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

a) Start with given T & $\{x_i\}$, Antonie constants, ε value for convergence.

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

calculate $P = \sum \frac{x_i \gamma_i P_i^S}{\hat{\phi}_i}$

c) calculate $\{y_i\}$ from $y_i = \frac{x_i \gamma_i P_i^S}{\hat{\phi}_i P}$

d) calculate $\{\phi_i\}$ from $\hat{\phi}_i = \exp \frac{B_{ii}(P - P_i^S) + \frac{1}{2} P \sum_j \sum_k y_i y_k (\delta_{ji} - \delta_{jk})}{RT}$

e) Calculat P_{new} from $P = \sum \frac{x_i \gamma_i P_i^S}{\hat{\phi}_i}$

f) if $\delta P < \varepsilon$. end at last P and $\{y_i\}$.

g) if $\delta P \geq \varepsilon$ go to step ⓒ and calculate new $\{\gamma_i\}$ with last $\{\hat{\phi}_i\}$.

Dew point pressure

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

a) start with T, $\{y_i\}$, Antonie constant and ε (error value).

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

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

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

Recalculate P.

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

c) calculate $\{x_i\}$ $x_i = \dfrac{y_i \phi_i P}{\gamma_i P_i^s}$

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

and use normalize $\{x_i\}$ to calculat $\{\gamma_i\}$

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

f) If $\Delta P < \varepsilon$. end with Last P & $\{x_i\}$

g) If $\Delta P > \varepsilon$. go to Step b)

Bubble Temperature

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

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

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

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

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

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

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

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

g) if $\Sigma k_i x_i < 1$ then $T_{last} < T_b$.

$$T_{new} = T_{last} \Sigma k_i x_i$$

and return to step c) and return to step b).

Dew temeperature

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 $\sum y_i/k_i > 1$. $T_{last} < T_d$.

$$T_{new} = T_{last} \sum y_i/k_i$$

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 $x_1 = 0.72$, respectively. Wlison equation is given as,

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

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

$$\begin{array}{cccccc} & & & j & & \\ & & 1 & 2 & 3 & 4 \\ & 1 & 1 & 2.3357 & 2.7385 & 0.4180 \\ i & 2 & 0.1924 & 1 & 1.6500 & 0.1108 \\ & 3 & 0.2419 & 0.5343 & 1 & 0.0465 \\ & 4 & 0.9699 & 0.9560 & 0.7795 & 1 \end{array}$$

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:

$$lnP^1{}_{sat}(kPa) = 16.58 - \frac{3638.37}{T(^oC) + 239.50} \qquad lnP^2{}_{sat}(kPa) = 16.90 - \frac{3795.17}{T(^oC) + 230.91}$$

$$lnP^3{}_{sat}(kPa) = 16.68 - \frac{3640.20}{T(^oC) + 219.61} \qquad lnP^4{}_{sat}(kPa) = 16.39 - \frac{3885.70}{T(^oC) + 230.17}$$

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 $lnP^i{}_{sat}(kPa)$ from Antoine equation wit the new value of T_b;

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

5. If $abs(T_b - T_i)$ <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®.

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

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

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.

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

	Methanol	Ethanol	Benzene	*p*-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
p-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

TABLE B.2 Binary Interaction Parameter b_{ij} for the NRTL Model for Selected Components

	Methanol	Ethanol	Benzene	*p*-Xylene	Toluene	Chloroform	Water	Acetone
Methanol	0.0	−1162.3	892.2	295.5	371.1	−71.9	173.0	114.1
Ethanol	483.8	0.0	−54.8	−1202.4	−113.5	−148.9	246.2	479.1
Benzene	−3282.6	882.0	0.0	122.7	1124.0	−375.4	591.4	−239.9
p-Xylene	1677.6	2504.2	−136.5	0.0	75.9	−17.7	296.7	173.6
Toluene	446.9	992.7	−863.7	−91.1	0.0	−57.0	14759.8	630.1
Chloroform	690.1	690.3	313.0	−120.2	−25.2	0.0	3240.7	−106.4
Water	−617.3	−586.1	−5954.3	−6046.0	−27269.4	−1140.1	0.0	420.0
Acetone	101.9	206.6	306.1	83.2	−400.5	−590.0	−1809.0	0.0

TABLE B.3 Binary Interaction Parameter c_{ij} for the NRTL Model for Selected Components

	Methanol	Ethanol	Benzene	*p*-Xylene	Toluene	Chloroform	Water	Acetone
Methanol	0.0	0.3	0.4	0.5	0.3	0.3	0.3	0.3
Ethanol	0.0	0.0	0.3	0.3	0.3	0.3	0.3	0.3
Benzene	0.0	0.0	0.0	0.3	0.3	0.5	0.2	0.3
p-Xylene	0.0	0.0	0.0	0.0	0.3	0.3	0.2	0.3
Toluene	0.0	0.0	0.0	0.0	0.0	0.3	0.2	0.3
Chloroform	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.3
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Acetone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE B.4 Antoine Equation Coefficients for Selected Components

	Methanol	Ethanol	Benzene	*p*-Xylene	Toluene	Chloroform	Water	Acetone
A	8.07240	8.1122	6.90565	6.99052	6.95464	6.93710	8.01767	7.23160
B	1574.990	1592.864	1211.033	1453.430	1344.800	1171.200	1715.7	1277.030
C	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.

$$\ln\left(P_i^{\mathrm{VAP}}\right) = A_i - \frac{B_i}{T + C_i} \tag{B.3}$$

Liquid-Liquid equilibria

A & B comprise the original binary mixture.

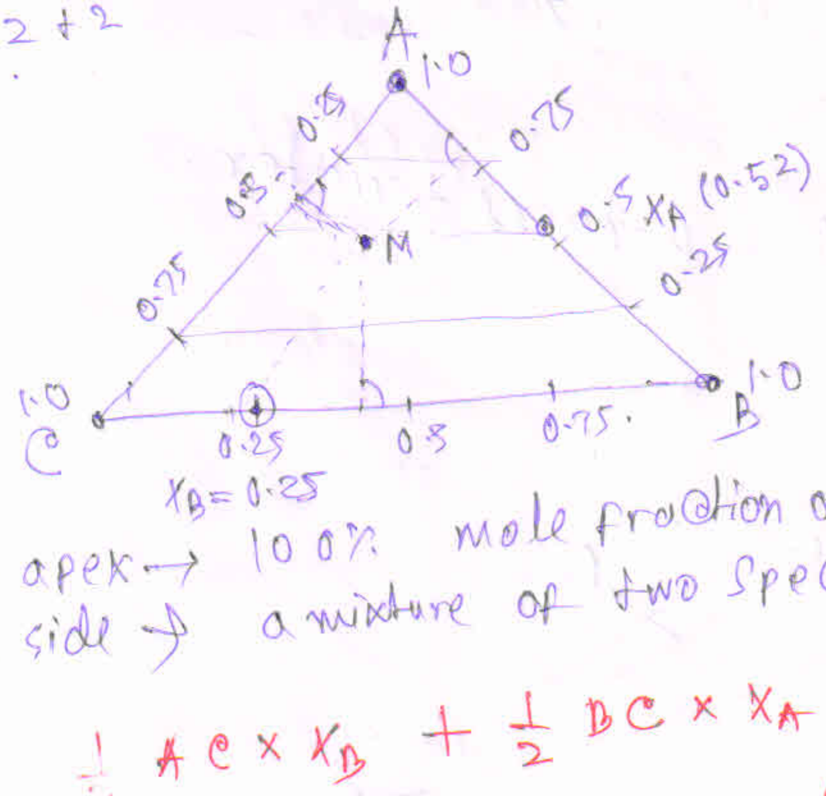
if A or B forms azeotrope or difference in volatility is very low.

The third solvent C is added to A & B, The solvent is paritially miscible or immiscible with original mixture or solution.

→ two liquid phase results.

Extract phase	Raffinate phase
↓	↓
Preferentially extract A	most of the B remains 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.

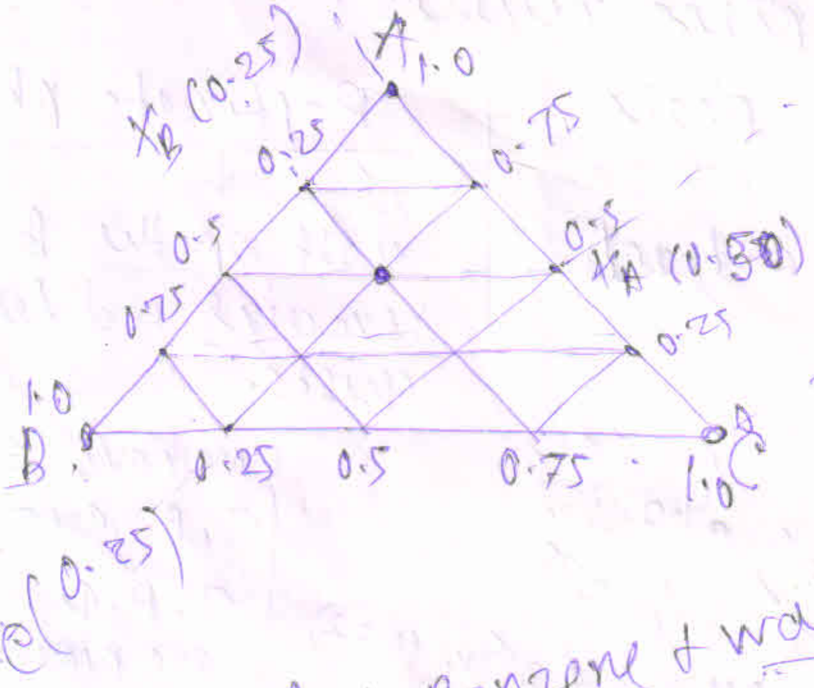
$$\frac{1}{2} AC \times x_B + \frac{1}{2} BC \times x_A + \frac{1}{2} AB \times x_C = \frac{1}{2} BC \times h$$

$AB = BC = AC = 1.$

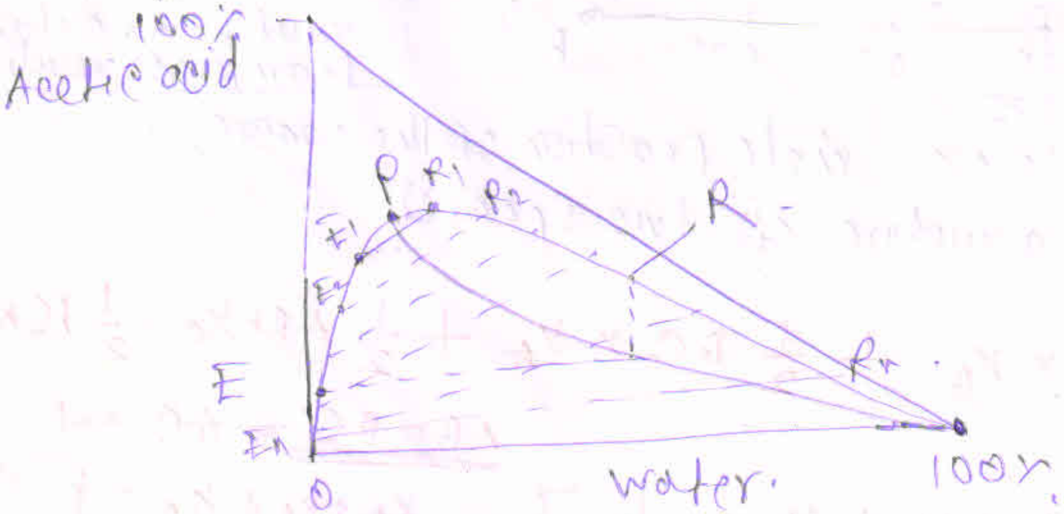
$$\therefore x_B + x_A + x_C = h \}$$

$x_A + x_B + x_C = 1$

[redacted]



Acetic acid + Benzene + water.



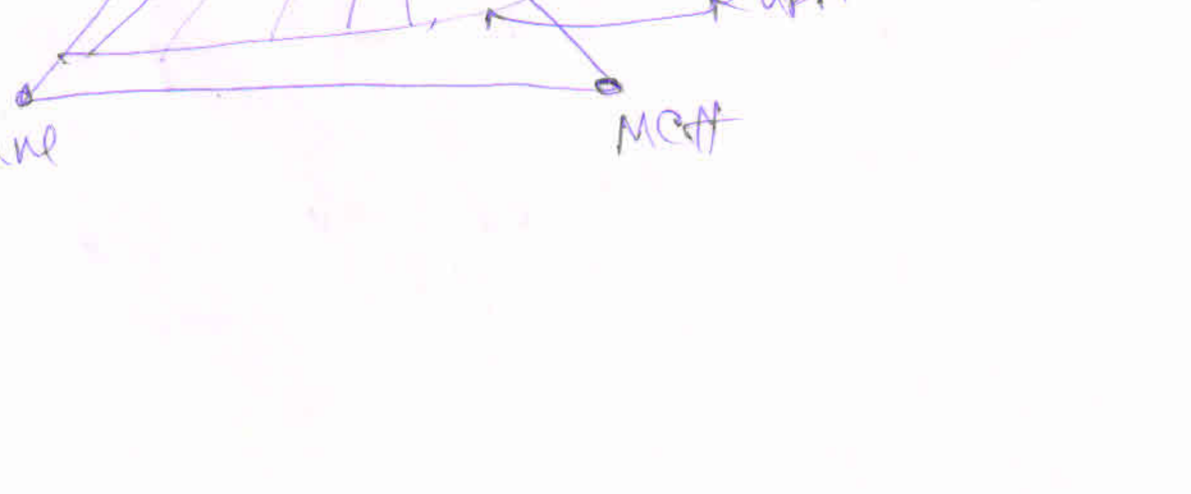
Type one   acetone-water-methyl isobutyl ketone.

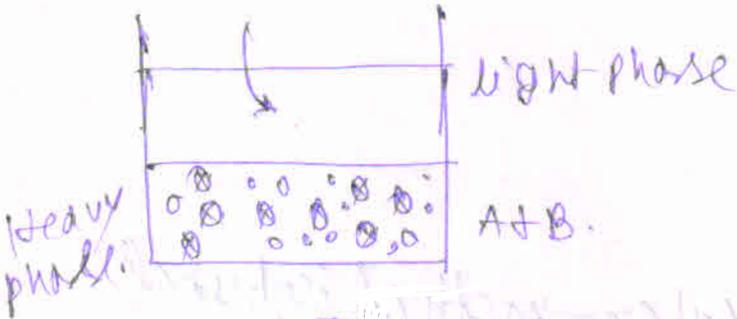
partial miscibility of solvent MIK & diluent water
complete " " " " & acetone (component to be extracted)

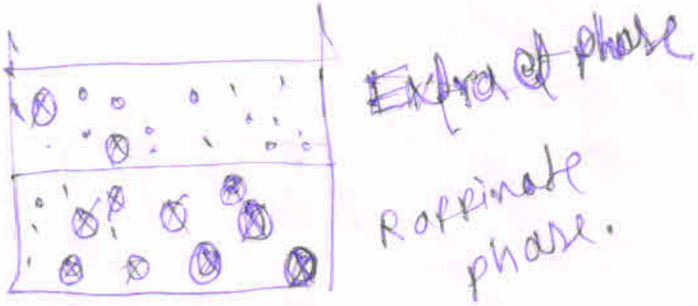
Type II

Aniline - n-heptane - methylcyclohexane (MCH).

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







$$\hat{f}_i^{I} = (x_i \varphi_i f_i)^{I}$$

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

at same T & P ; at equilibrium.

$$\hat{f}_i^{I} = \hat{f}_i^{II}$$ (pure component fugacities)

$$\hat{f}_i^{I} = \hat{f}^{II}$$

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

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

$$\Sigma x_i^{I} = 1 \; ; \; \Sigma x_i^{II} = 1$$

x_1^{I}, x_2^{I}

x_1^{II}, x_2^{II}

$\varphi = f(x)$.