Lectures 10

Computational Methods in Thermodynamics

O'Connell & Haile
Chapter 11

Topics:

- Types of phase equilibrium problems
  - Several VLE cases: Bubble / Dew / Flash
- Logic diagrams for solution strategies
- Solving reaction equilibria cases
- Simultaneous phase & reaction equilibrium problems

PHASE EQUILIBRIUM CASES

For phase equilibria, have $\mathcal{C}$ - $\mathcal{P}$ + 2 independent variables among $(\mathcal{C}-1)\mathcal{P}+2$ (T, P, $\{x'\}$, $\{x''\}$, . . .);
Other $(\mathcal{P}-1)\mathcal{C}$ variables from $(\mathcal{P}-1)\mathcal{C}$ fugacity equations

$$f_i'(T,P,\{x'\}) = f_i''(T,P,\{x''\}) = \ldots i = 1,\ldots,\mathcal{C}$$

Many problem choices, usual ones for VLE:

Problem Name in VLE Situations	Knowns	Unknowns to Find
Bubble-T	P and $\{x^\alpha\}$	T and $\{x^\beta\}$
Dew-T	P and $\{x^\beta\}$	T and $\{x^\alpha\}$
Bubble-P	T and $\{x^\alpha\}$	P and $\{x^\beta\}$
Dew-P	T and $\{x^\beta\}$	P and $\{x^\alpha\}$
Flash	T, P, and $\{z\}$	$\{x^\alpha\}$, $\{x^\beta\}$, N^β/N

FFF Choice of Liquid Sets Strategy I.

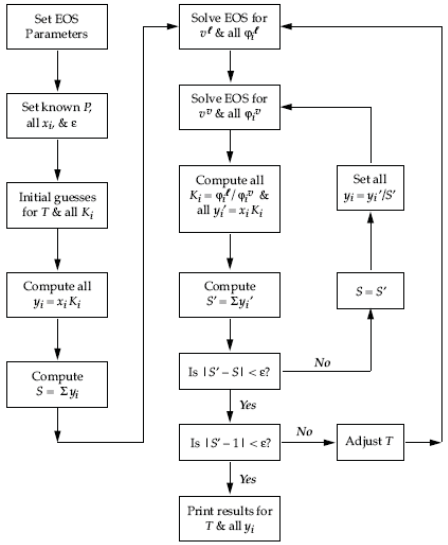
***K*- factor for ϕ–ϕ Method from rearrangement of fugacity relations**

$$K_i \equiv \frac{y_i}{x_i} = \frac{\phi_i^l(T,v^l,\{x\})}{\phi_i^v(T,v^v,\{y\})} \qquad i = 1,\ldots,\mathcal{C}$$

Also must solve for v^v & v^l; 2 more eqs.

$$P = P(T,v^l,\{x\}) = P(T,v^v,\{y\})$$

Logic Diagram for ϕ -ϕ Bubble-T



FFF Choice of Liquid Sets Strategy II.

***K*-factor for γ -ϕ Method from rearranged fugacity relations (FFF#1, #5)**

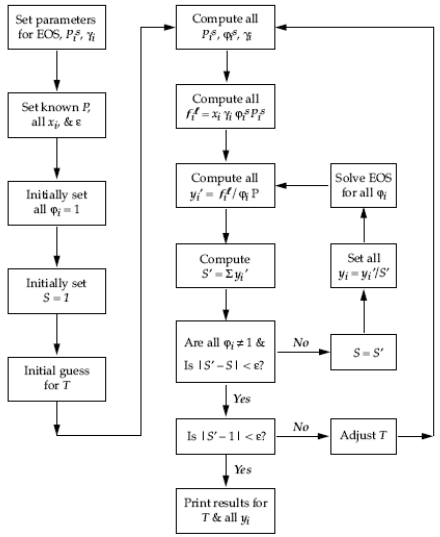
$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i(T,\{x\}) f_i^0(T) \exp\left[\int_{P_i^0}^{P} \frac{\bar{V}_i^l(T,P,\{x\})}{RT} d\pi\right]}{\phi_i^v(T,v^v,\{y\})P} \qquad i = 1,\ldots,\mathcal{C}$$

Low pressure, set $\exp[\ \ ] \sim 1$, $f_i^0 = \phi_i^s(T) P_i^s(T)$
& use 2nd Virial EoS for $\phi_i^v(T,P,\{y\}), \phi^s(T)$

$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i(T,\{x\})\phi_i^s(T)P_i^s(T)}{\phi_i^v(T,P,\{y\})P} \qquad i = 1,\ldots,\mathcal{C}$$

Solving easier than ϕ-ϕ, but has model mismatch at critical point ($\gamma_i \neq \phi_i$)

Logic Diagram for γ–ϕ Bubble-T



Solution to γ–γ Via Rachford-Rice Flash

LLE is $\mathcal{F}$' problem with $\mathcal{C}$+1 independent & 2$\mathcal{C}$-1 dependent variables among:
***T*, *P*, {*z*}, {x^a}, {x^b}, $R \equiv N^b/(N^a+N^b)$**

Solve $\mathcal{C}$ fugacity eqs. & $\mathcal{C}$-1 material bals.

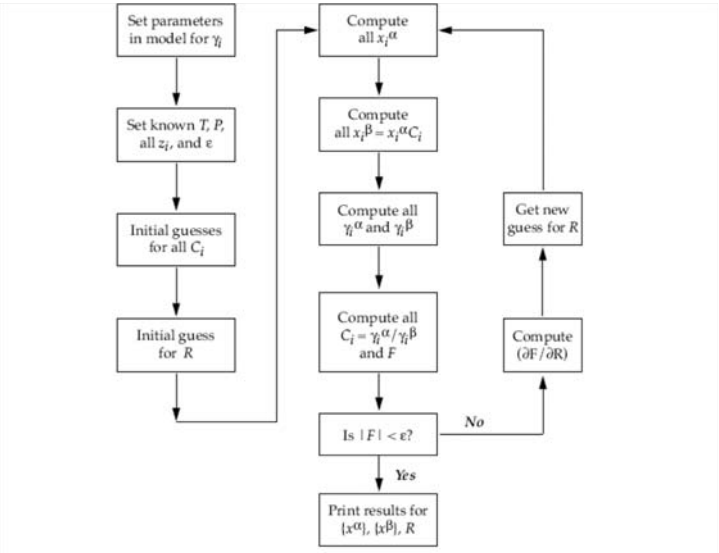
Transform to $\mathcal{C}$+1 equations in $\mathcal{C}$+1 variables;

{C_i}, *R* $C_i = \frac{x_i^\beta}{x_i^\alpha} = \frac{\gamma_i^\alpha(T,\{x^\alpha\})}{\gamma_i^\beta(T,\{x^\beta\})}$; $\sum_{i=1}^{C} \frac{z_i(C_i-1)}{1+R(C_i-1)} = 0$

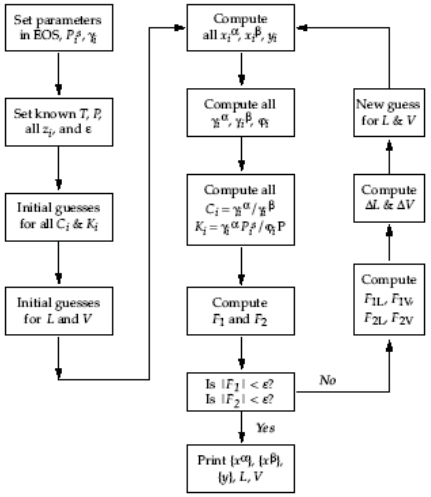
with compositions

$$x_i^\alpha = \frac{z_i}{1+R(C_i-1)}; \qquad x_i^\beta = \frac{z_i C_i}{1+R(C_i-1)}$$

Logic Diagram for Rachford-Rice Flash



Double Rachford-Rice (γ–γ, γ–ϕ) for VLLE



Reaction Equilibria Via 2 Methods

1-Phase (Sec. 11.2), stoichiometric form uses Singular Value Decomposition & Newton-Raphson search for $\mathcal{R}$, $\{x^{eq}\}$ from T, P, Δg_{if}^0, f_i / f_i^0 model (Fig. 11.7)

In multiphase, use Rachford-Rice & SVD

Summary has advice on solving problems

MULTIPHASE, MULTIREACTION CASE

