Chapter 14. Topics in Phase Equilibrium

The simplest models for vapor/liquid equilibrium

- **Raoult's law** $y_i P = x_i P_i^{sat}$

- **Henry's law** $y_i P = x_i H_i$ => for a species whose $T_c <= T$ of applicants

- **Modified Raoult's law** $y_i P = x_i \gamma_i P_i^{sat}$ => Applied only to low pressure

14.1. The γ / φ formulation of VLE.

Extension of modified Raoult's Law
$\Rightarrow$ Overcome the limitation of modified Raoult's Law
$\Rightarrow$ Introduce vapor-phase fugacity to explain nonideality

From eqn (11.52) $\hat{f}_i^v = y_i \hat{\phi}_i P$ => Vapor phase

From eqn (11.90) $\hat{f}_i^l = x_i \gamma_i f_i$ => Liquid phase

at equilibrium $\hat{f}_i^v = \hat{f}_i^l$

$$\therefore y_i \hat{\phi}_i P = x_i \gamma_i f_i$$

From eqn (11.44)
$$f_i = \varphi_i^{sat} P_i^{sat} \exp[\frac{V_i^l(P - P_i^{sat})}{RT}]$$

$$y_i \hat{\varphi}_i P = x_i \gamma_i \hat{\varphi}_i^{sat} P_i^{sat} \exp[\frac{V_i^l(P - P_i^{sat})}{RT}]$$

$$\Rightarrow y_i \frac{\hat{\varphi}_i}{\hat{\varphi}_i^{sat}} \exp[-\frac{V_i^l(P - P_i^{sat})}{RT}]P = x_i \gamma_i P_i^{sat}$$

$$\Rightarrow y_i \Phi P = x_i \gamma_i P_i^{sat} \quad \text{(14.1)} \quad \Rightarrow \text{gamma/phi formulation}$$

Usually poynting factor ≈ 1 $\qquad \Rightarrow \Phi_i \approx \frac{\hat{\varphi}_i}{\varphi_i^{sat}}$ (14.2)

If $\Phi_i = \gamma_i = 1$ $\qquad \Rightarrow$ (14.1) becomes raoult's Law

If $\Phi_i = 1$ $\qquad \Rightarrow$ (14.1) becomes modified Raoult's Law

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○ To use eqn(14.1) for the analysis of VLE => need to know the value of $P_i^{sat}, \Phi_i, \gamma_i$

1) φ_i^{sat} => obtained by the Antoine eqn

$$\ln P_i^{sat} = A_i - \frac{B_i}{T + C_i} \qquad (14.3)$$

2) Φ_i => need to obtain $\hat{\varphi}_i$ and φ_i^{sat}

$$\hat{\varphi} = \exp \frac{P}{RT}[B_{ii} + \frac{1}{2} \sum_j \sum_k y_i y_k (2\delta_{ji} - \delta_{jk})] \qquad (14.4)$$

Values of the pure species vivial coeff. of the species in the mixture (11.69) ~ (11.74)

$\hat{\varphi}_i^{sat}$: fugacity coeff for pure i as a saturated vapor in eqn(14.4) $\delta_{ji}, \delta_{jk} = 0$

$$\varphi_i^{sat} = \exp \frac{B_{ii} P_i^{sat}}{RT}$$

$$\therefore \Phi_i = \frac{\hat{\varphi}_i}{\hat{\varphi}_i^{sat}} = \exp \frac{B_{ii}(P - P_i^{sat}) + \frac{1}{2} P \sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk})}{RT} \qquad (14.6)$$

(14.5)

For a binary system comprised of species 1 and 2, this becomes

$$\Phi_1 = \exp \frac{B_{11}(P - P_1^{sat}) + Py_2^2 \delta_{12}}{RT} \qquad (14.7a)$$

$$\Phi_2 = \exp \frac{B_{22}(P - P_2^{sat}) + Py_1^2 \delta_{12}}{RT} \qquad (14.7b)$$

3) γ_i : can be obtained from the various models (Van Laar, Wilson, UNIFAC, etc ..)

○ **Dew point and Bubble point Calculation using Gamma/Phi formulations => need iteration**

$$\Phi_i = \Phi(T, P, y_1, y_2, \cdots, y_{N-1})$$

$$\gamma_i = \gamma(T, x_1, x_2, \cdots, x_{N-1})$$

$$P_i^{sat} = f(T)$$

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{\Phi_i P} \quad (14.8) \qquad\qquad x_i = \frac{y_i \Phi_i P}{\gamma_i P_i^{sat}} \quad (14.9)$$

since $\displaystyle\sum x_i = 1, \ \sum y_i = 1$

$$P = \sum_i \frac{x_i \gamma_i P_i^{sat}}{\Phi_i} \quad (14.10) \qquad\qquad P = \frac{1}{\displaystyle\sum_i \frac{y_i \Phi_i}{\gamma_i P_i^{sat}}} \quad (14.11)$$

1) BUBL P calculation

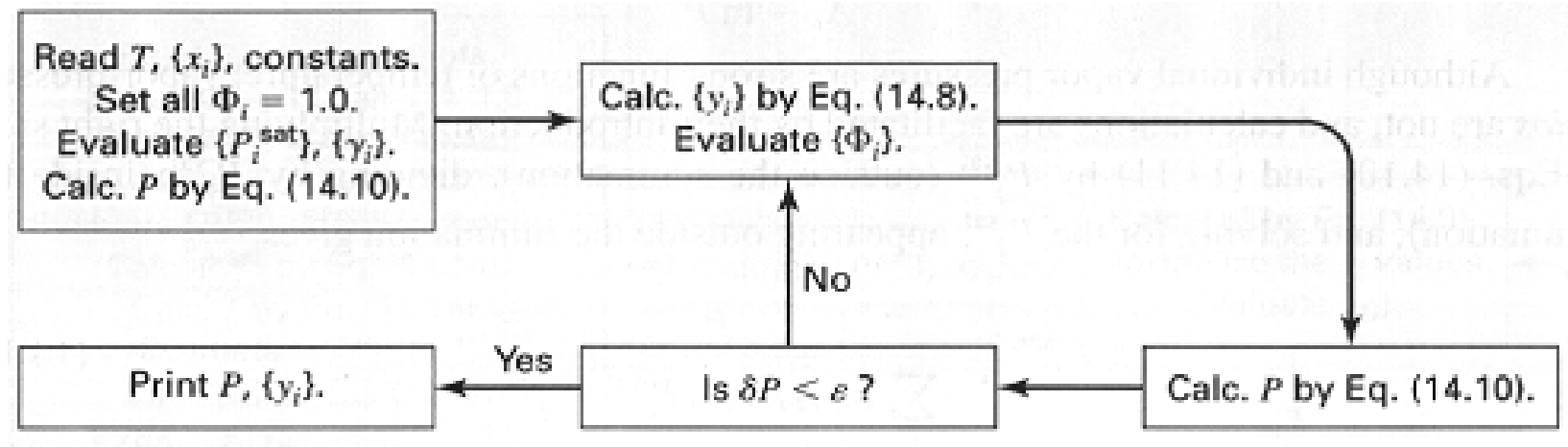=> Calculation (y_i) and P , given x_i and T

Bubble P calculations

Fig. 14.1 Block diagram for the calculation BUBL P

Read T, $\{x_i\}$, constants. Set all $\Phi_i = 1.0$. Evaluate $\{P_i^{sat}\}$, $\{\gamma_i\}$. Calc. P by Eq. (14.10).

Calc. $\{y_i\}$ by Eq. (14.8). Evaluate $\{\Phi_i\}$.

No

Calc. P by Eq. (14.10).

Is $\delta P < \varepsilon$?

Yes

Print P, $\{y_i\}$.

2) Dew P calculation

=> Calculation x_i and P , given y_i and T

– BUBL P and Dew P calculation : temperature is given => can calculate P_i^{sat}

– BUBL T and Dew T : T is unknown => need initial estimate for T to do iteration

i) $T = \sum_i x_i T_i^{sat}$ (for BUBL T) $T = \sum_i y_i T_i^{sat}$ (for Dew T)

where $\quad T_i^{sat} = \dfrac{B}{A_i - \ln P} - C_i$ (14.12)

ii) Multiply eqn(14.10) (14.11) by P_i^{sat} (outside summation) and didice by P_i^{sat} (inside summation)

$$P_j^{sat} = \frac{P}{\sum_i (x_i \gamma_i / \varphi_i)(P_i^{sat} / P_j^{sat})} \quad (14.13) \qquad P_j^{sat} = P \sum_i \frac{y_i \varphi_i}{\gamma_i}\left(\frac{P_j^{sat}}{P_i^{sat}}\right) \quad (14.14)$$

iii) Calculate corresponding T from eqn(14.3)

$$T = \frac{B_j}{A_j - \ln P_j^{sat}} - C_j$$

Dew P calculations

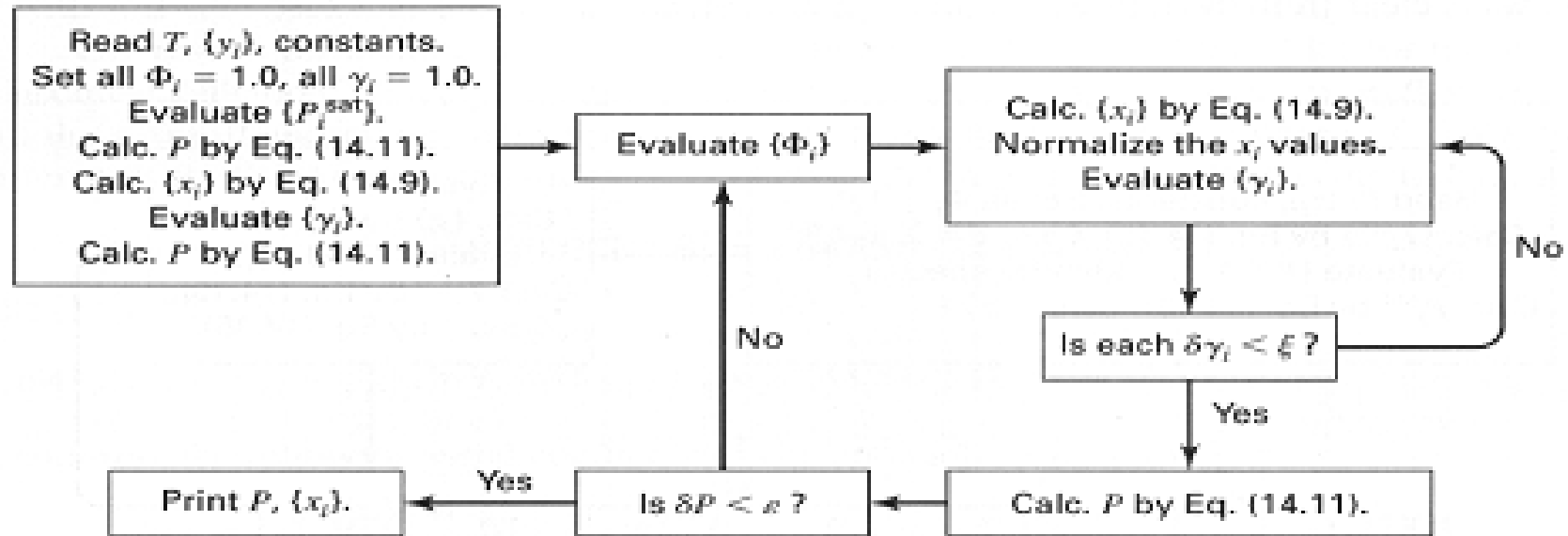Fig. 14.2 Block diagram for the calculation DEW P.

BUBL T calculation

=> Calculate (y_i, T) given x_i and P

Read P, $\{x_i\}$, constants. Set all $\Phi_i = 1.0$.
Calc. $\{T_i^{sat}\}$ by Eq. (14.12). Calc. $T = \sum_i x_i T_i^{sat}$.
Evaluate $\{P_i^{sat}\}$, $\{\gamma_i\}$. Identify species j.
Calc. P_j^{sat} by Eq. (14.13). Calc. T by Eq. (14.15).

Evaluate $\{P_i^{sat}\}$.
Calc. $\{y_i\}$ by Eq. (14.8).
Evaluate $\{\Phi_i\}$, $\{\gamma_i\}$.
Calc. P_j^{sat} by Eq. (14.13).
Calc. T by Eq. (14.15).

No

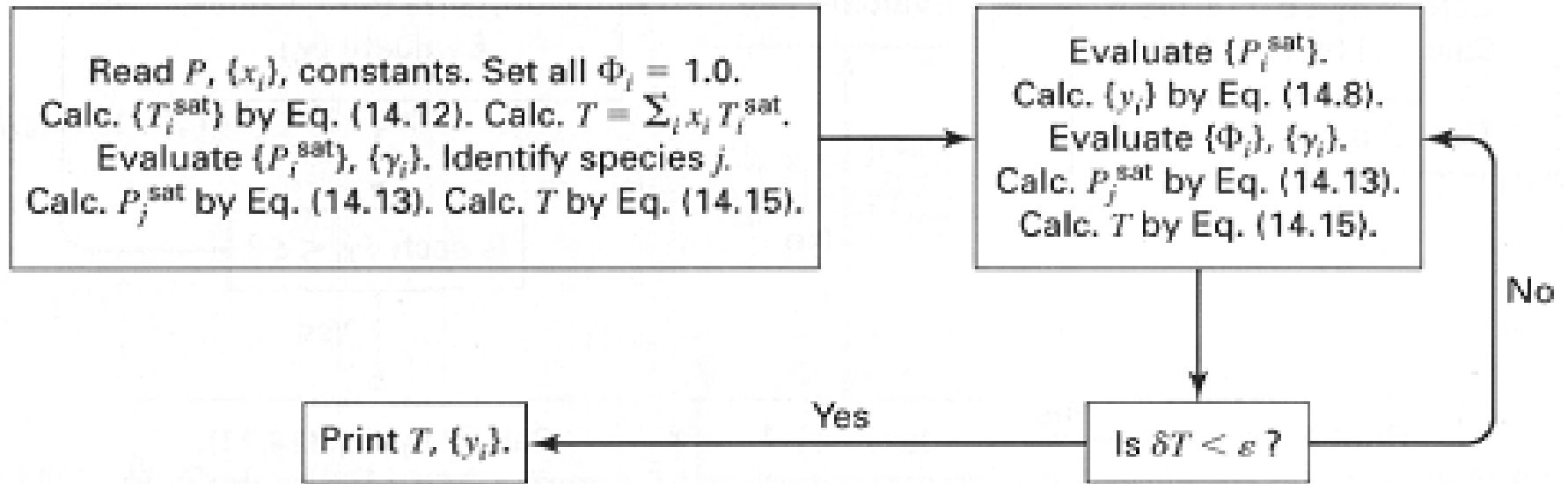Print T, $\{y_i\}$.

Yes

Is $\delta T < \varepsilon$?

Fig. 14.3 Block diagram for the calculation BULB T.

DEW T calculation

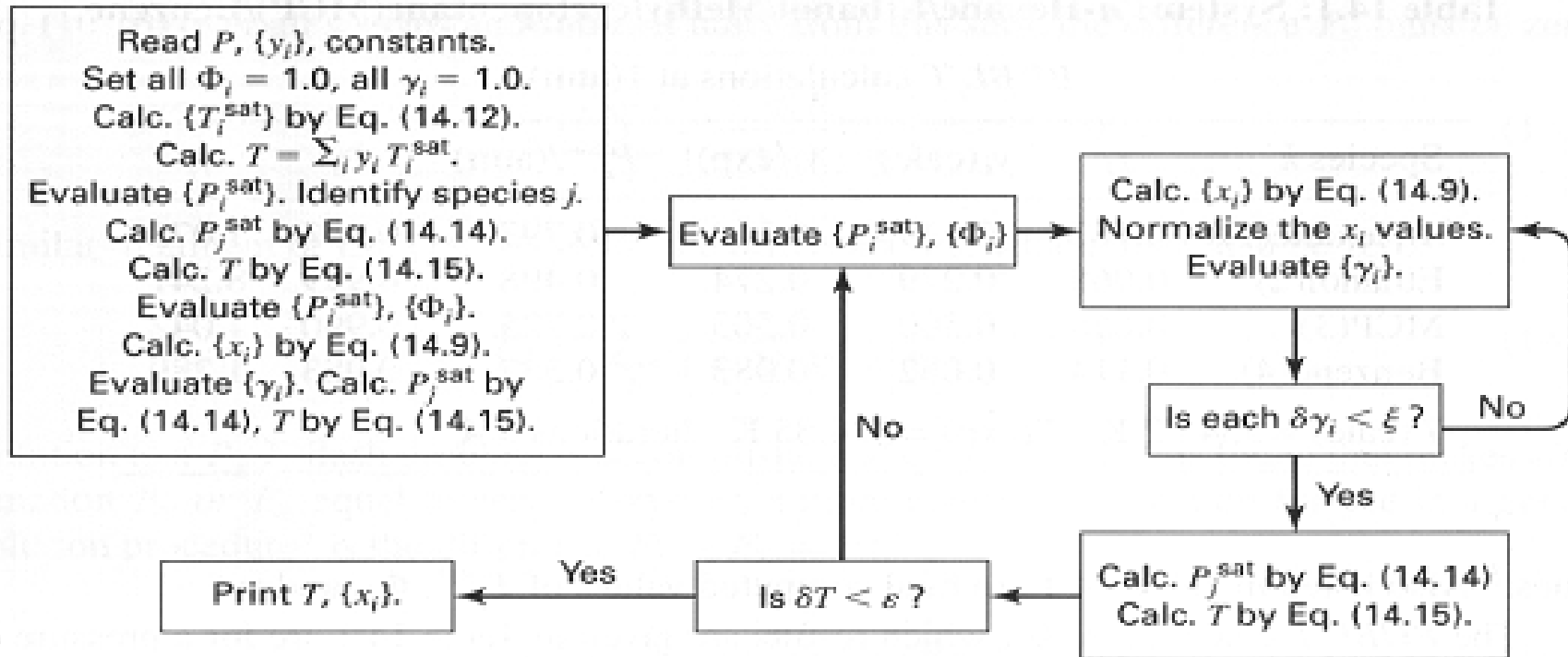=> Calculate (x$_i$, T) given y$_i$ and P

Fig. 14.4 Block diagram for the calculation DEW T.

Flash calculation

In chap 10. Flash calculation is based on Raoult's law and K-value correlation
=> Use the gamma/phi formulation

$$y_i = \frac{z_i K_i}{1 + v(K_i - 1)} \qquad (i = 1, 2, \cdots, N) \qquad \text{(10.16)}$$

$$x_i = \frac{z_i}{1 + v(K_i - 1)} \qquad (i = 1, 2, \cdots, N)$$

First, $\Sigma y_i = 1, \ \Sigma y_i - 1 = 0 = F_y$

$$F_y = \sum_i \frac{z_i K_i}{1 + v(K_i - 1)} - 1 = 0 \qquad \text{(14.17)}$$

Second, $\Sigma x_i = 1, \ \Sigma x_i - 1 = 0 = F_x$

$$F_x = \sum_i \frac{z_i}{1 + v(K_i - 1)} - 1 = 0 \qquad \text{(14.18)}$$

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14.2 VLE from Cubic Equation of State

For VLE, $\hat{f}_i^v = \hat{f}_i^l$ (11.48)

Since, $\hat{\varphi}_i = \dfrac{\hat{f}_i}{x_i P}$, $y_i P \hat{\varphi}_i^v = x_i P \hat{\varphi}_i^l$ $\Rightarrow$ $y_i \hat{\varphi}_i^v = x_i \hat{\varphi}_i^l$

○ Vapor pressure for a pure species

- Usually P_i^{sat}, can be obtained by experimental measurement

- P_i^{sat} at equilibrium can be obtained using EOS

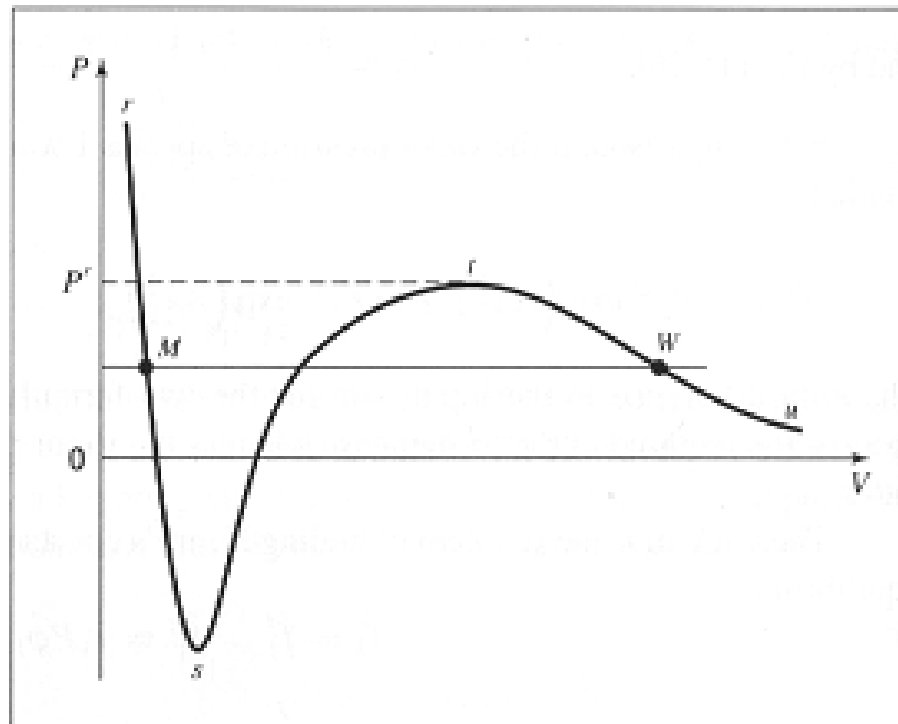   Generic Cubic Equation of state

$$P = \frac{RT}{v-b} \times \frac{a(T)}{(v+\varepsilon b)(v+b)}$$

   If P –> ∞ , V –> b , if P –> 0, V –> ∞

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Fig. 14-7

Figure 14.7: Isotherm for $T < T_c$ on PV diagram for a pure fluid.

- For pure species, $\ln \varphi_i^v = \ln \varphi_i^l \rightarrow \ln \varphi_i^l - \ln \varphi_i^v = 0$

   and $\hat{\varphi}_i = \varphi_i(T, P)$

- For a saturated liquid or vapor $P \rightarrow P^{sat}$ in that case $\varphi_i = \varphi_i(T, P_i^{sat})$

   where $P_i^{sat} = f(T)$

- Two widely used cubic eqn of state

   $\left[\begin{array}{l} \text{Sorve / Redlich / kwung (SPK) eqn} \\ \text{Peng/Robinson (PR) eqn} \end{array}\right.$

- $\left[\begin{array}{l} \text{Vapor \& vapor-like Roots of the Generic Cubic EOS (use } v = \dfrac{ZRT}{P} \text{)} \\ \\ \qquad Z_i = 1 + \beta_i - q_i \beta_i \dfrac{Z_i - \beta_i}{(Z_i - \varepsilon\beta_i) + (Z_i + \varepsilon\beta_i)} \qquad \text{(3.52)} \rightarrow \text{(14.31)} \\ \\ \text{Liquid \& liquid -like Roots of the Generic Cubic EOS} \end{array}\right.$

$$Z_i = \beta_i + (Z_i + \varepsilon\beta_i)(Z_i + \sigma\beta_i)\frac{1 + \beta_i - Z_i}{q_i\beta_i} \qquad \text{(3.56)} \rightarrow \text{(14.35)}$$

   Parameter : eqn (3.45), (3.46), (3.50), (3.51)
(a_i, b_i, β_i, q_i)

Pure number : $\varepsilon, \sigma, \Psi, \Omega, \alpha(Tr_i)$ => Table 3.1

From (11.37) $\quad \ln \varphi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \qquad$ (11.37)

– Procedure to obtain P_i^{sat} for pure for a give T, P

   1) Calculate $\quad Z_i^l - dZ_i^v \quad$ using eqn (14.35)(14.36) before that, calculate parameters

   2) Using eqn(11.37), calculate $\quad \ln \varphi_i^l, \ln \varphi_i^v \quad$ before that, calculate q_i, I_i

   3) Check if $\quad \ln \varphi_i^l - \ln \varphi_i^v = 0$

     If yes, P –> P^{sat}, if no, iteration
     Eqn for calculating vapor pressure –> table 14.3

14.3 Equilibrium and Stability

If system ⇔surrounding => thermal and mechemical equilibrium heat exchange (Q) and expansion work (w) are reversible.

Under these circumstance

$$dS_{surr} = \frac{dQ_{surr}}{T_{surr}} = \frac{-dQ}{T}$$
dQ : heat transfer for system
T : system = T_{surr}

By **thermodynamic 2ⁿᵈ law** , $dS^t + dS_{surr} \geqslant 0$

$$\Rightarrow dS^t - \frac{dQ}{T} \geqslant 0 \qquad \therefore dQ \leqslant TdS^t \qquad \text{(14.65)}$$

By **thermodynamic 1ˢᵗ law**

$$dU^t = dQ + dW = dQ - PdV^t \Rightarrow dQ = dU^t + PdV^t$$

$$dU^t + PdV^t \leqslant TdS^t \rightarrow dU^t + PdV^t - TdS^t \leqslant 0 \qquad \text{(14.66)}$$

Inequality : apply to every incremental change of the system between
nonequilibrium states

equality : holds for changes between equilibrium states (reversible)

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eqn(14.61) : too general to apply to practical problem
=> need more restricted version

$$(dU^t)_{S^t, V^t} \leqslant 0 \quad \text{or} \quad (dS^t)_{U^t, V^t} \geqslant 0$$

At const, T, P

$$dU^t + PdV^t - TdS^t \leqslant 0 \;\Rightarrow\; d(U^t + PV^t - TS^t)_{T,P} \leqslant 0$$

$$G^t = H^t - TS^t = U^t + PV^t - TS^t$$

$$\therefore d(G^t)_{T,P} \leqslant 0 \qquad \text{(14.67)}$$

○ Determination of equilibrium states

1) Express G^t as a function of the numbers of moles of the species in the several phases

2) Finds the set of values for mole number that minimize G^t subject to the constraints of mass conversion

$$\text{At equilibrium} \quad d(G^t)_{T,P} = 0 \qquad \text{(14.68)}$$

At constant T, P, $\Delta G, \Delta G', \Delta G''$ must be continuous function of x_1, and the

$\Delta G'' > 0$ => Criterion of stability for single-phase

$$\therefore \frac{d^2 \Delta G}{dx_1^2} > 0 \quad \text{(const. T, P)}$$

and $\quad \dfrac{d^2(\Delta G/RT)}{dx_1^2} > 0 \quad$ (const. T, P) $\qquad$ (14.65)

From eqn(12.30) $\quad G^E = \Delta G - RT \sum x_i \ln x_i$

$$\frac{\Delta G}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{G^E}{RT} \qquad \therefore \frac{d(\Delta G/RT)}{dx_1} = \ln x_1 - \ln x_2 + \frac{d(G^E/RT)}{dx_1}$$

$$\frac{d^2(\Delta G/RT)}{dx_1} = \frac{1}{x_1 x_2} + \frac{d^2(G^E/RT)}{dx_1^2} > 0$$

$$\therefore \frac{d^2(G^E/RT)}{dx_1^2} > -\frac{1}{x_1 x_2} \quad (\text{const } T, P) \qquad \text{(14.65)}$$

From eqn(12.6) $\dfrac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$

$$\Rightarrow \frac{d(G^E/RT)}{dx_1} = \ln \gamma_1 - \ln \gamma_2 + x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = \ln \gamma_1 - \ln \gamma_2$$

zero $\Rightarrow$ Gibbs–Duhem eq.

$$\Rightarrow \frac{d^2(G^E/RT)}{dx_1^2} = \frac{d \ln \gamma_1}{dx_1} - \frac{d \ln \gamma_2}{dx_1} = \frac{1}{x_2} \frac{d \ln \gamma_1}{dx_1}$$

In combination with eqn(14.70)

$$\frac{d \ln \gamma_1}{dx_1} > -\frac{1}{x_1} \quad \text{(const T, P)}$$

$$\frac{d\hat{f}_1}{dx_1} > 0 \quad , \quad \frac{d\mu_1}{dx_1} > 0 \quad (\text{const } T, P)$$