

CHAPTER V

APPLICATION OF THE SELECTED EOS FOR MULTICOMPONENT SYSTEMS

5.1 MIXING RULES

In applying the Leiva equation to multicomponent VLE, usual mixing rule for obtaining the two constants for the gas mixture ;

$$a_{\text{mix}} = \sum_i^n \sum_j^n y_i y_j (a_i a_j)^{0.5} (1 - K_{ij}) \quad (5.1)$$

$$b_{\text{mix}} = \sum_i^n y_i b_i \quad (5.2)$$

were employed. The same rules were used for the liquid mixtures with x replacing y in these equations.

Once the mixing rules Equations (5.1) and (5.2) are chosen, the fugacity coefficient of any component i in a vapor mixture from Leiva's equation can be calculated by the equation

$$\ln \phi_i^V = b_i(Z-1)/b - \ln(Z-B) - \frac{A}{B} \left[2 \sum_{j=1}^n \frac{x_j a_j}{a} - \frac{b_j}{b} \right] \ln(1+B/z) \quad (5.3)$$

where $Z = PV/RT$

$$A = \frac{aP}{(RT)^2}, \quad B = \frac{bP}{RT}$$



The same expression applies to calculate for the liquid fugacity coefficient $\phi_i^L = f_i^L / x_i P$ by replacing y of equation 5.3 with x .

At equilibrium:

$$f_i^V = f_i^L \quad (5.4)$$

$$K_i = \frac{\phi_i^L}{\phi_i^V} = y_i / x_i \quad (5.5)$$

Equations 5.1 - 5.5 are those used for VLE calculations

5.2 BINARY INTERACTION PARAMETERS (K_{ij})

For the calculation of K -ratios in multicomponent mixtures, it is necessary to have not only parameter a_i and b_i for each pure component but also an interaction parameter K_{ij} for each binary pair in the mixture.

Compilations of K_{ij} values applicable to the van der Waals family have been made by Chueh and Prausnitz [8] and other developers of the various equations in the form of Equation 4.1. For the most accurate results, however, the values of K_{ij} must be determined for binary pairs in the mixture by fitting to the experimental data for the pair. For a mixture containing N components, the binaries will be $N(N-1)/2$. When there are no binary data, K_{ij} values may be estimated by plotting known values against various molecular parameters, as shown by Gum, Yamada, and Whitman [27].

5.3 EVALUATION OF OPTIMAL BINARY INTERACTION PARAMETERS ($K_{ij,opt}$)

In practice, values of K_{ij} were determined by an optimization technique, fitting K_{ij} to experimental equilibrium data by minimizing the difference between the calculated and experimental values of a selected equilibrium property. Properties of particular interest in phase equilibrium calculations include bubble point pressure, dew point pressure, bubble point temperature, dew point temperature, and equilibrium K ratios. It would be impractical to minimize the errors in the model with respect to all of these properties.

A number of criteria have been used for the evaluation and are as follow:

- (1) minimization of deviation in predicted K values [29, 30, 31]
- (2) minimization of deviation in predicted bubble point pressures [5, 28, 32, 33, 34]
- (3) minimization of deviations in predicted bubble point vapor composition [28]
- (4) minimization of the flash volume variance [5]
- (5) minimization of the sum of variances of the flash vapor and liquid compositions [35].

According to Kato [28] and Graboski and Daubert [5], the best criterion for selecting the optimum interaction parameter is a minimization of bubble pressure variance, as defined

$$S_p = \sum_{n=1}^{n_p} \left[\frac{P(T, X)^E - P^E}{P^E} \right]^2 \quad (5.6)$$

where n_p = number of points
 superscript E = experimental value
 $P(T, X)^E$ = the calculated pressure corresponding to the liquid composition X at T.

To evaluate interaction parameters to be used in multicomponent Vapor-Liquid equilibria for the Leiva EOS, equation (5.6) was used in two search procedures. In the first, a search procedure bracketed the desired value and in the second a Fibonacci search technique was used to determine the optimum interaction parameter. The range of this parameter to begin the search procedure is from 0.0 to 0.3. A schematic diagram outlining the calculation is given in Figure 5.1.

Binary P-X-T data were used in this study. The calculated pressures and vapor phase compositions for each data point were evaluated through a bubble point calculational routine from the given values of temperature and liquid phase composition. The complete computer program is shown in the appendix.

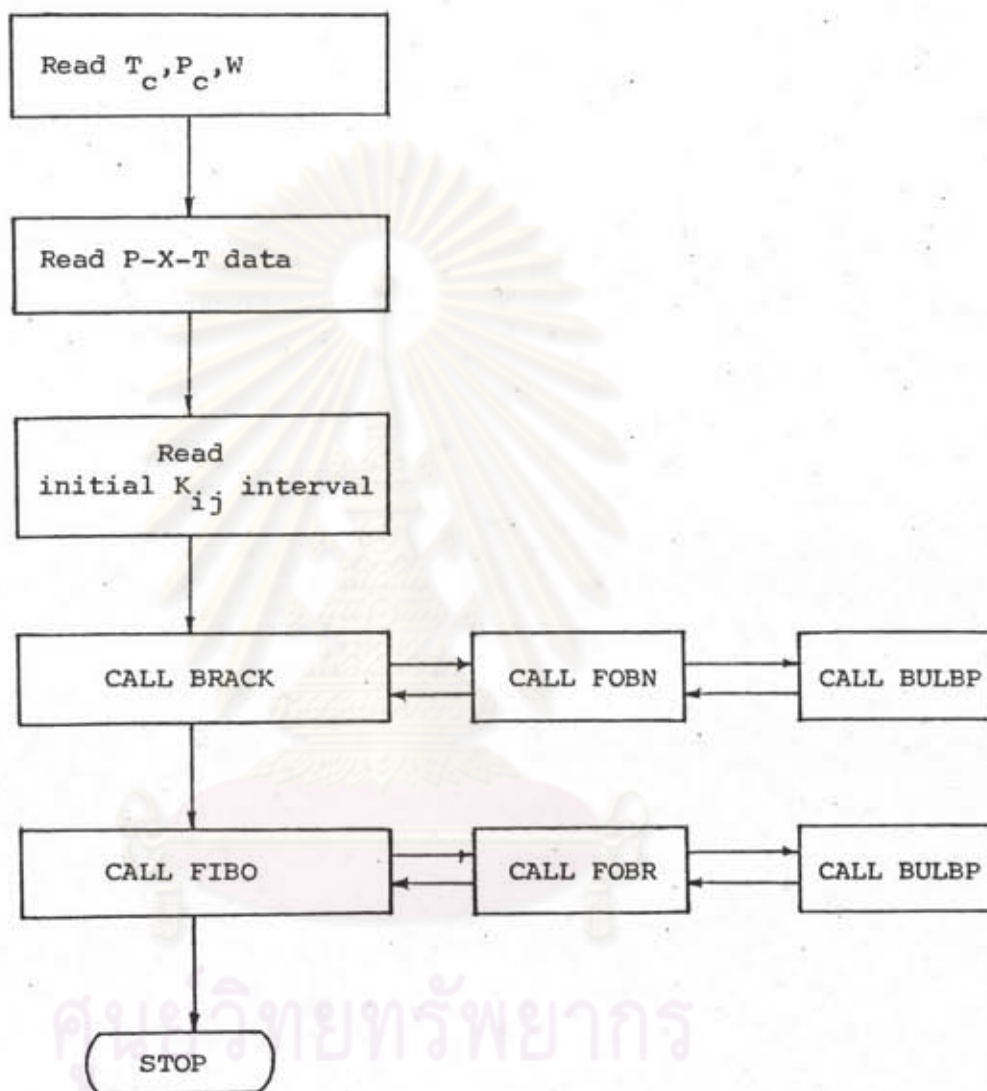
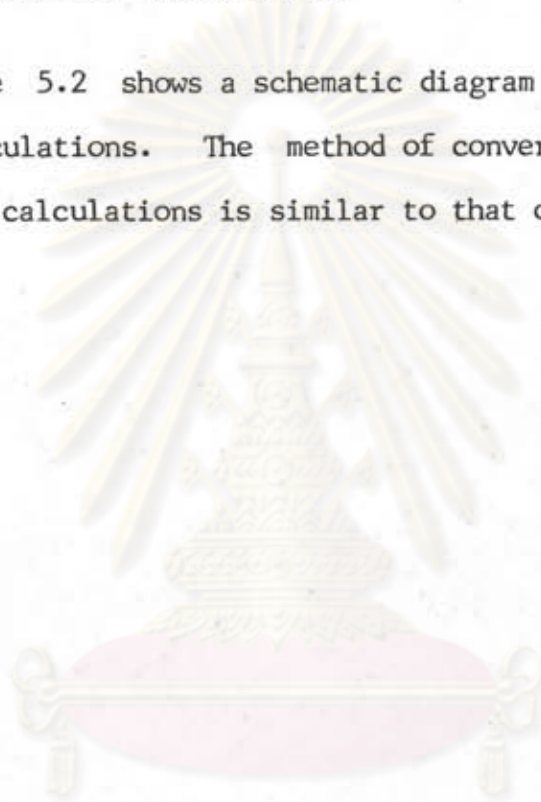


figure 5.1 Flow Diagram for Evaluating Interaction Parameter.

5.4 PREDICTION OF MULTICOMPONENT PHASE EQUILIBRIA : BUBBLE POINT PRESSURE CALCULATIONS

In applying the Leiva equation of state for the prediction of multicomponent phase equilibria at high pressure, the bubble point pressure calculations were studied.

Figure 5.2 shows a schematic diagram for the bubble point pressure calculations. The method of convergence used for the bubble point calculations is similar to that of Cheuh and Prausnitz [8].



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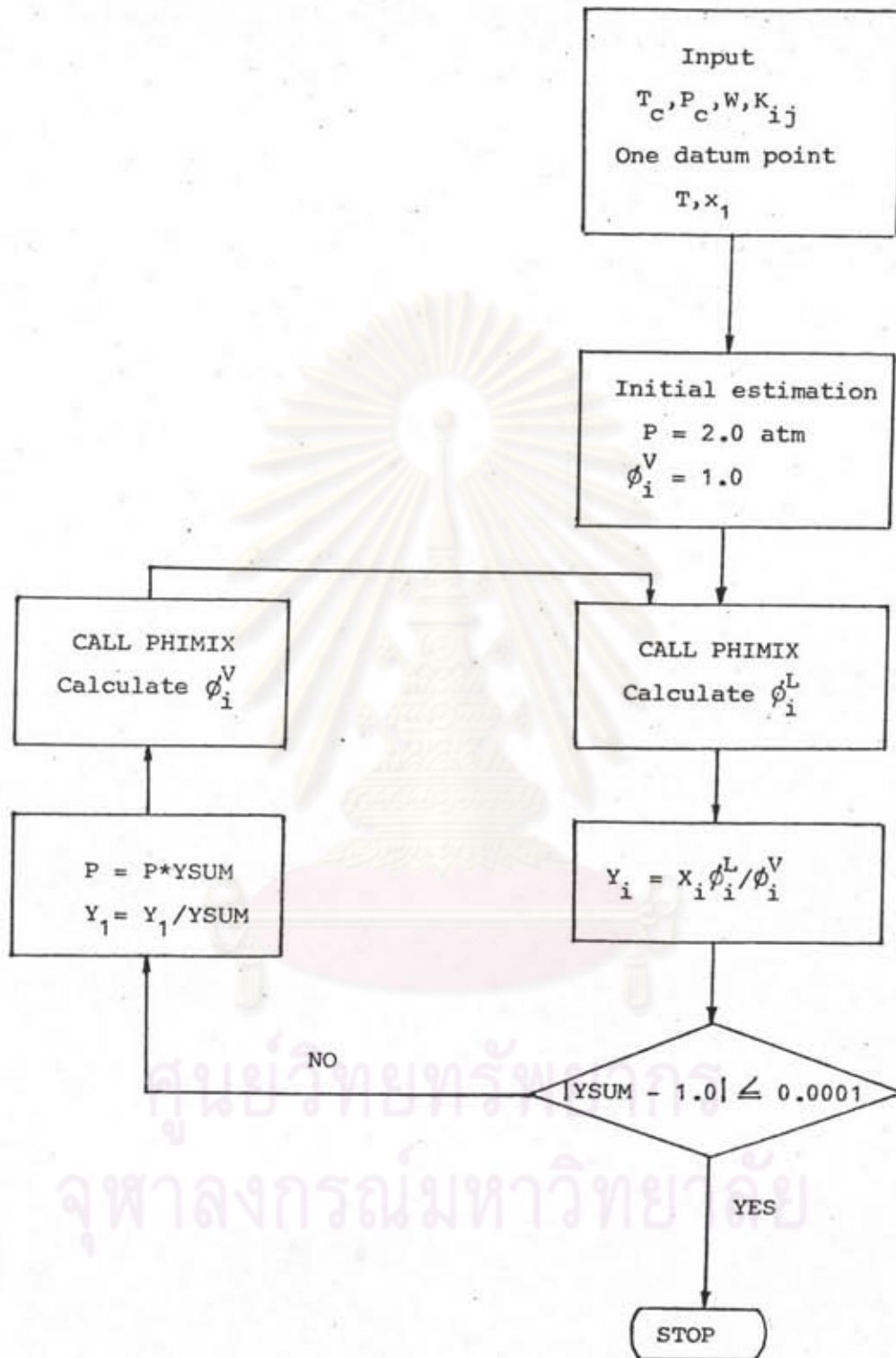
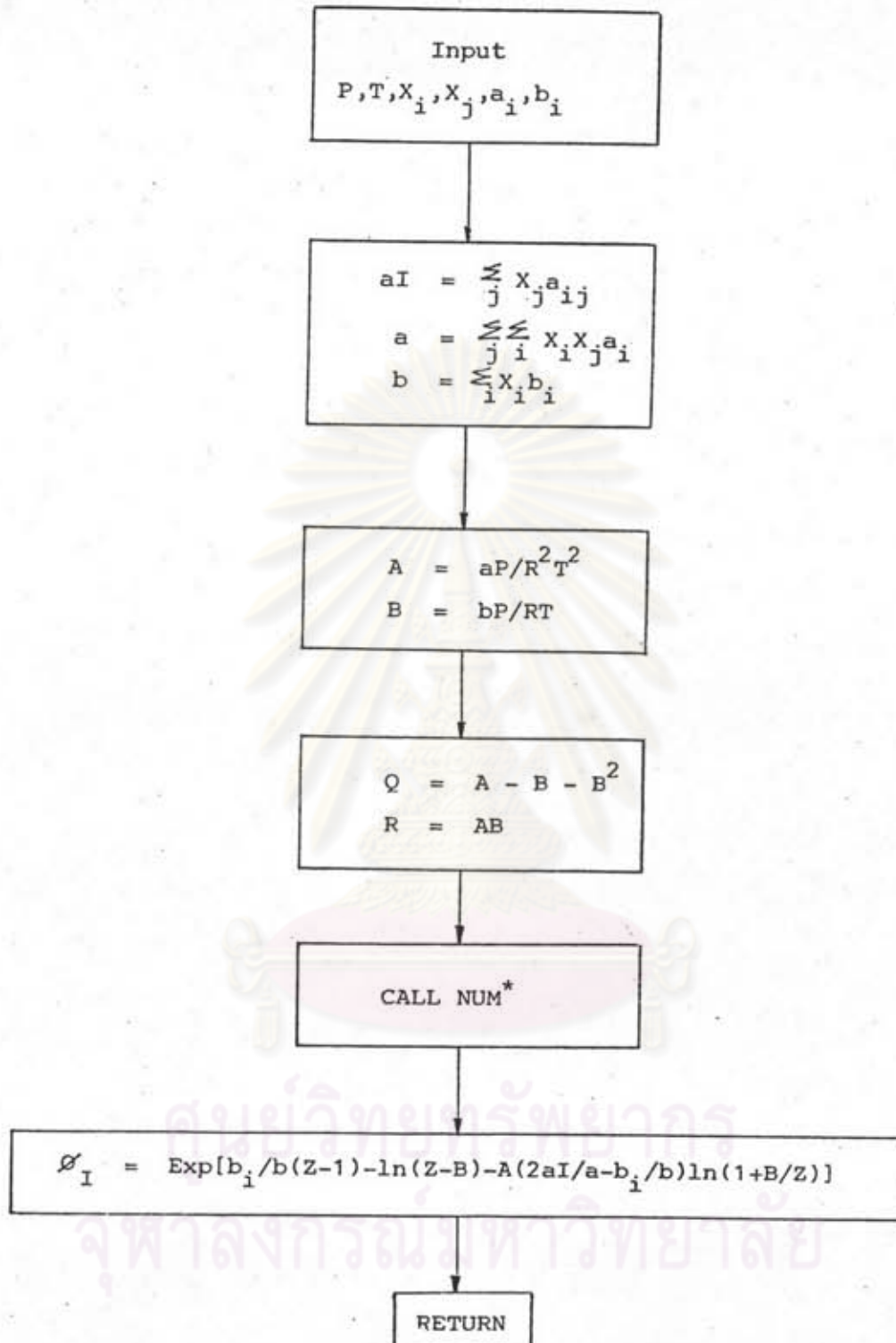


figure 5.2 Flow Diagram for Bubble Point Pressure Calculation

(SUBROUTINE BULBP)



* NUM : Subroutine for cubic equation solution

figure 5.3 Flow Diagram for Subroutine PHIMIX.

Table 5.1 Physical Properties of Pure Components [1]

Components	P_c, atm	T_c, K	ω
N ₂	33.5	126.2	0.040
Methane	45.4	190.6	0.008
CO ₂	72.8	304.2	0.225
Ethane	48.2	305.4	0.098
Propane	41.9	369.8	0.152
n-Butane	37.5	425.2	0.193
n-Pentane	33.3	469.6	0.251
Hexane	29.3	507.4	0.296
Heptane	27.0	540.2	0.351
Octane	24.5	568.8	0.394
Nonane	22.8	594.6	0.444
Decane	21.3	617.6	0.400
Undecane	19.4	638.8	0.535
Dodecane	18.0	658.3	0.562
Tridecane	17.0	675.8	0.623

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