

## CHAPTER V

### DETERMINATION OF BINARY INTERACTION PARAMETER

This chapter describes evaluation of binary interaction parameters by using back calculation method and other mathematical method such as Newton-Raphson. Computer programs were written in PASCAL. Flow charts of the program and algorithm are also presented.

#### 5.1 Back Calculation Method

When experimental data on density or molar volume ( $V_{exp}$ ), pressure and temperature of a binary system are available, the parameter  $k_{ij}$  in the cubic equation of state can be determined by back calculation.

The objective function used is

$$\frac{1}{N} \sum_{i=1}^N \left| \frac{V_{cal}[i] - V_{exp}[i]}{V_{exp}[i]} \right| \quad (5.1)$$

where  $N$  is number of experimental data points and  $V_{cal}$  is calculated molar volume from equation of state. The mathematical tools required are the Newton-Raphson method and the region elimination method.

#### 5.2 Mathematics Method

This section describes the mathematical tools that used in the program as follows:

##### 5.2.1 Newton-Raphson Method

In the solution of positive roots of cubic equations of state, the Newton-Raphson method is used widely. This method differs from other methods in that the method is

employed by which successive approximations to the solution  $x$  of an equation  $f(x) = 0$  are calculated as

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \quad (5.2)$$

and solution is found when

$$|x_{n+1} - x_n| < \varepsilon \quad (5.3)$$

for some suitable small value of  $\varepsilon$

## 5.2.2 Region Elimination Method

Region elimination methods for a one-dimensional search make it possible to delete a calculated portion of the range of  $x$  from consideration on each successive stage of the search for an extremum of  $f(x)$ . When the remaining subinterval is sufficiently small, the search terminates.

The basic element underlying region elimination methods is the comparison of values of  $f(x)$  at two or more points within the range of  $x$ . Moreover, assume that  $f(x)$  is unimodal and has a minimum within the interval. The most efficient region elimination methods such as the Fibonacci and Golden Section search methods use a constant ratio for dividing the interval into segments.

### 5.2.2.1 Golden Section Search Method

The golden section method which evolved from the Fibonacci numbers. The strategy employed in the golden section search is to locate the two interior points so that the interval eliminated on one iteration will be of the same proportion to the total interval regardless of the interval length. In addition, only one new point has to be calculated at each iteration.

For any particular interval  $L^k$ , if  $a^k$  and  $b^k$  are the current bounds of the interval at stage  $k$  in the search, then the two interior points are located at  $x_1^k = a^k + 0.382 \cdot L^k$  and

$x_2^k = a^k + 0.618 * L^k$ . In Figure 5.1, note that  $f(x_1^k) > f(x_2^k)$ , hence at the next step  $a^{k+1} = x_1^k$  and  $b^{k+1} = b^k$ . The left interior point  $x_1^{k+1}$  replaces  $x_2^k$ , and then selects the right interior point as  $x_2^{k+1} = b^{k+1} - 0.382(b^{k+1} - a^{k+1})$ .

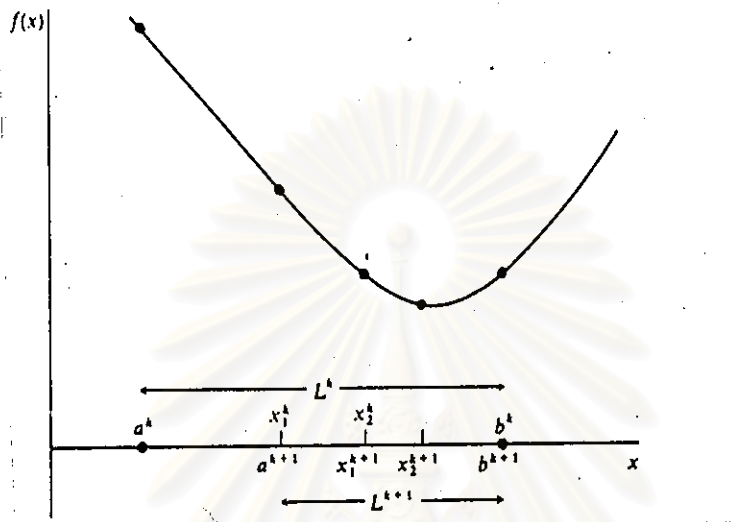


Figure 5.1 Selection of interior points in golden section search.

### 5.3 Computer Program

This section describes input data and algorithm of the program including the simple flow chart as follows:

#### 5.3.1 Input Data

The data which are required in the program are listed as follows:

1. Constant variable: Gas constant
2. Substances: benzene, cyclohexane, n-heptane.

3. Thermodynamic properties: critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), acentric factor ( $\omega$ ), pure compound parameter ( $\kappa_p, \kappa_2, \kappa_3$ ).
4. Experimental data: temperature, pressure, molar volume of mixtures ( $V_{exp}$ ), number of components, number of experimental data ( $N$ ).
5. Initial binary interaction parameter interval: upper limit ( $bk$ ), Lower limit ( $ak$ ).

### 5.3.2 Algorithm of the Programs

A simplified algorithm of the program is listed below. Figure 5.2 illustrates flow chart of the program.

1. Input all the data mentioned in section 5.3.1.
2. Dividing the  $k_{ij}$  interval by using golden section search method mentioned in section 5.2.2.1.
3. Calculation of  $V_{cal}$  in Subprogram by using Newton-Raphson method. Note that, initial value of  $Z$  equals 0.0 for liquid phase and 1.0 for vapor phase. Figure 5.3, 5.4 and 5.5 illustrate the flow chart of Subprogram Func EOS; Func PR, Func PRSV and Func PRSV2, and Func MRK respectively.
  - If equation is PR EOS, go to Subprogram Func PR.
  - If equation is PRSV EOS, go to Subprogram Func PRSV.
  - If equation is PRSV2 EOS, go to Subprogram Func PRSV2.
  - If equation is MRK EOS, go to Subprogram Func MRK.
4. Calculation the objective function (OBF) is defined by the expression:
 
$$OBF = \frac{1}{N} \sum_{i=1}^N \left| \frac{V_{cal}[i] - V_{exp}[i]}{V_{exp}[i]} \right| \quad (5.4)$$
5. Check if the OBF of  $d_1$  point is more than the OBF of  $d_2$  point:
  - If the answer is 'YES',  $d_1$  point equals  $ak$  point.
  - If the answer is 'NO',  $d_2$  point equals  $bk$  point.
6. Check if the absolute difference between  $d_1$  and  $d_2$  is less than 0.0001:

- If the answer is 'NO', go to step 2.
- If the answer is 'YES', go to step 7.

7. Calculate  $k_y$  from the equation below:

$$k_y = \frac{d_1 + d_2}{2} \quad (5.5)$$

8. Write optimum  $k_y$

9. Calculation of molar volume by Subprogram Func Volume. Figure 5.7 illustrates the flow chart of Subprogram Func Volume.

9.1 Input optimum  $k_y$ .

9.2 Calculation of molar volume, go to step 3 and then go to step 10.

10. Calculation of percentage average absolute deviation (%AAD) as follows:

$$\%AAD = \frac{100}{N} \sum_{i=1}^N \left| \frac{V_{cal}[i] - V_{exp}[i]}{V_{exp}[i]} \right| \quad (5.6)$$

11. Write molar volume of each composition and percentage average absolute deviation (%AAD).

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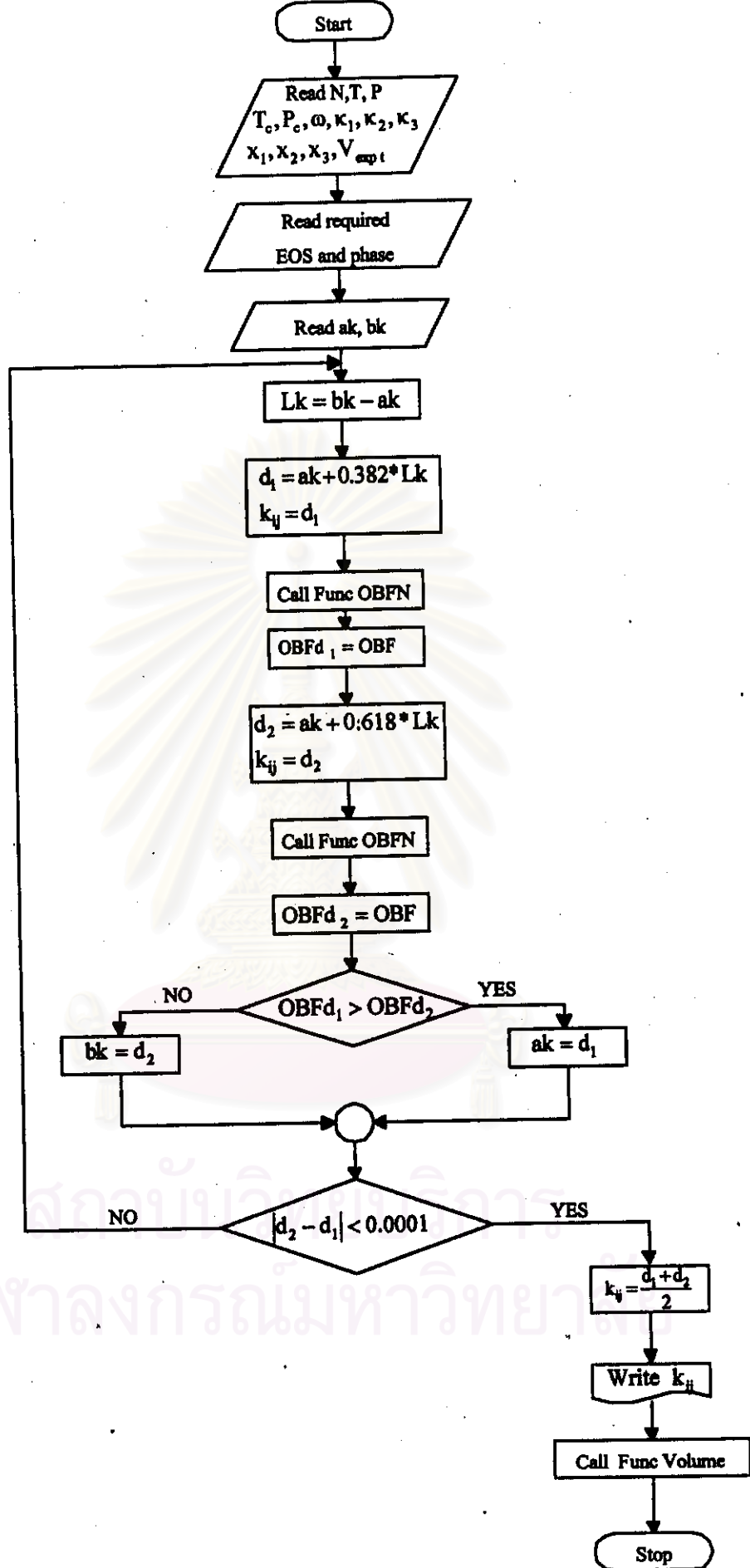


Figure 5.2 Flow chart of the program.

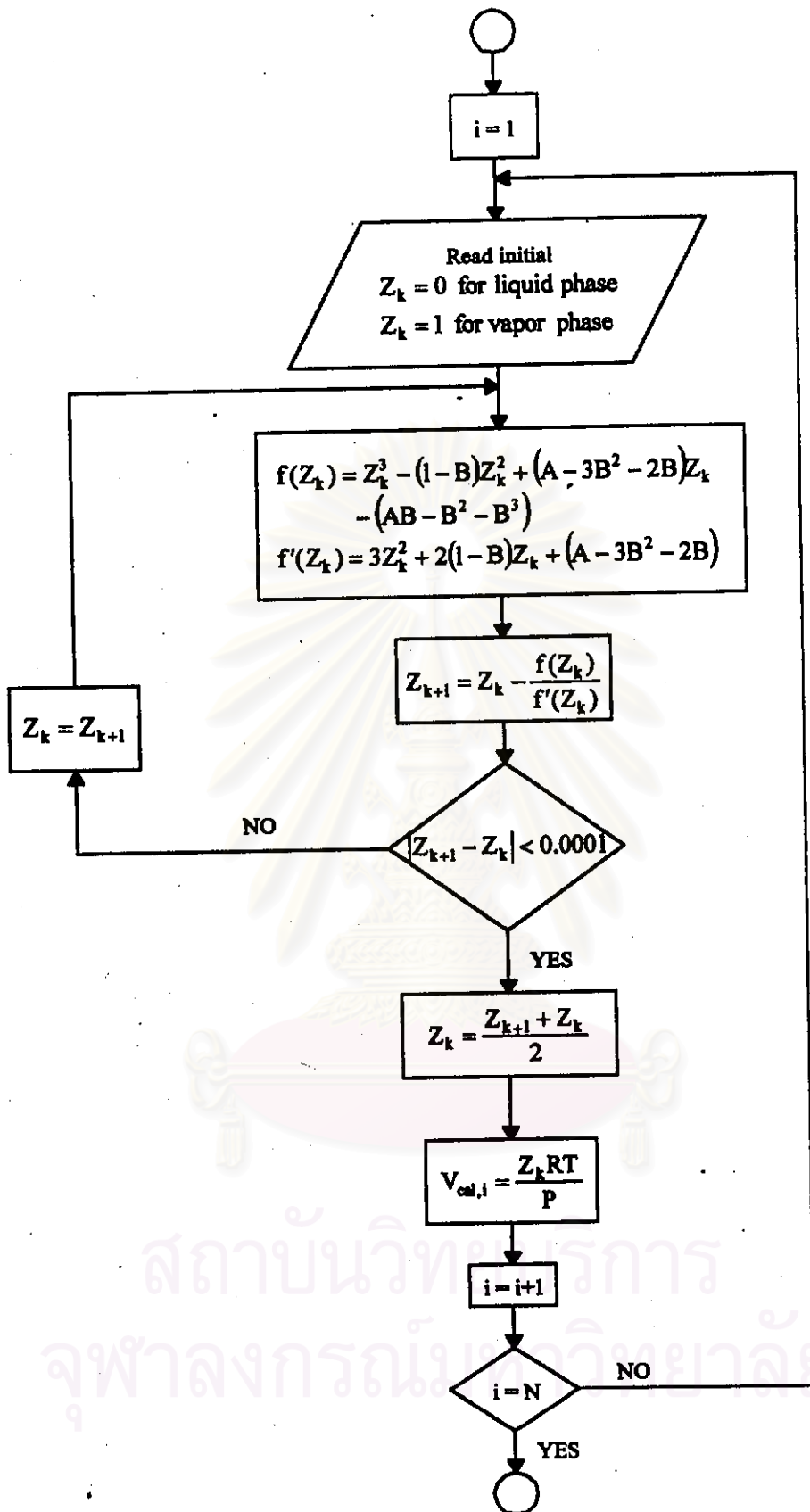


Figure 5.3 Flow chart of subprogram Func PR.

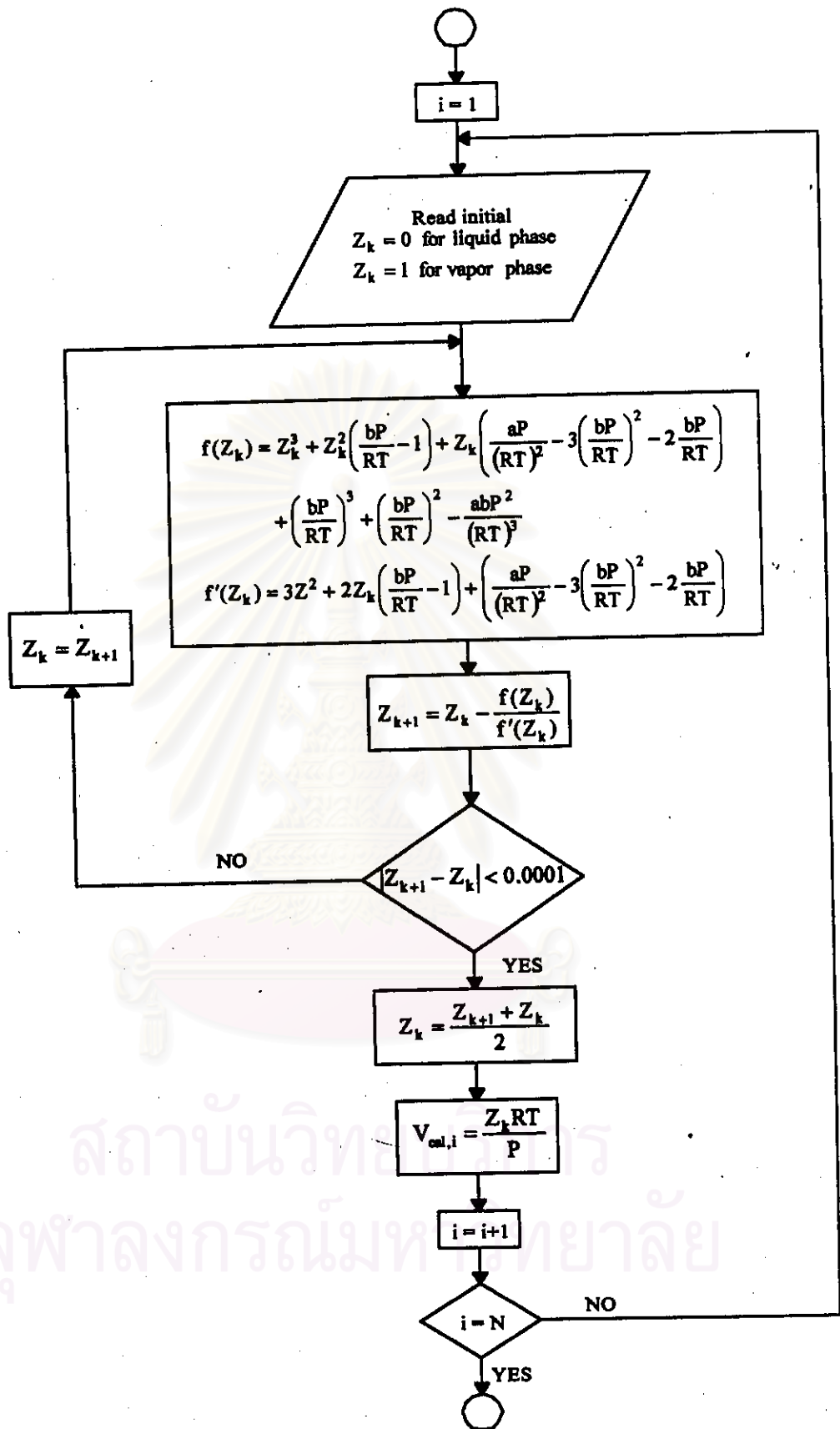


Figure 5.4 Flow chart of subprogram Func PRSV and PRSV2.



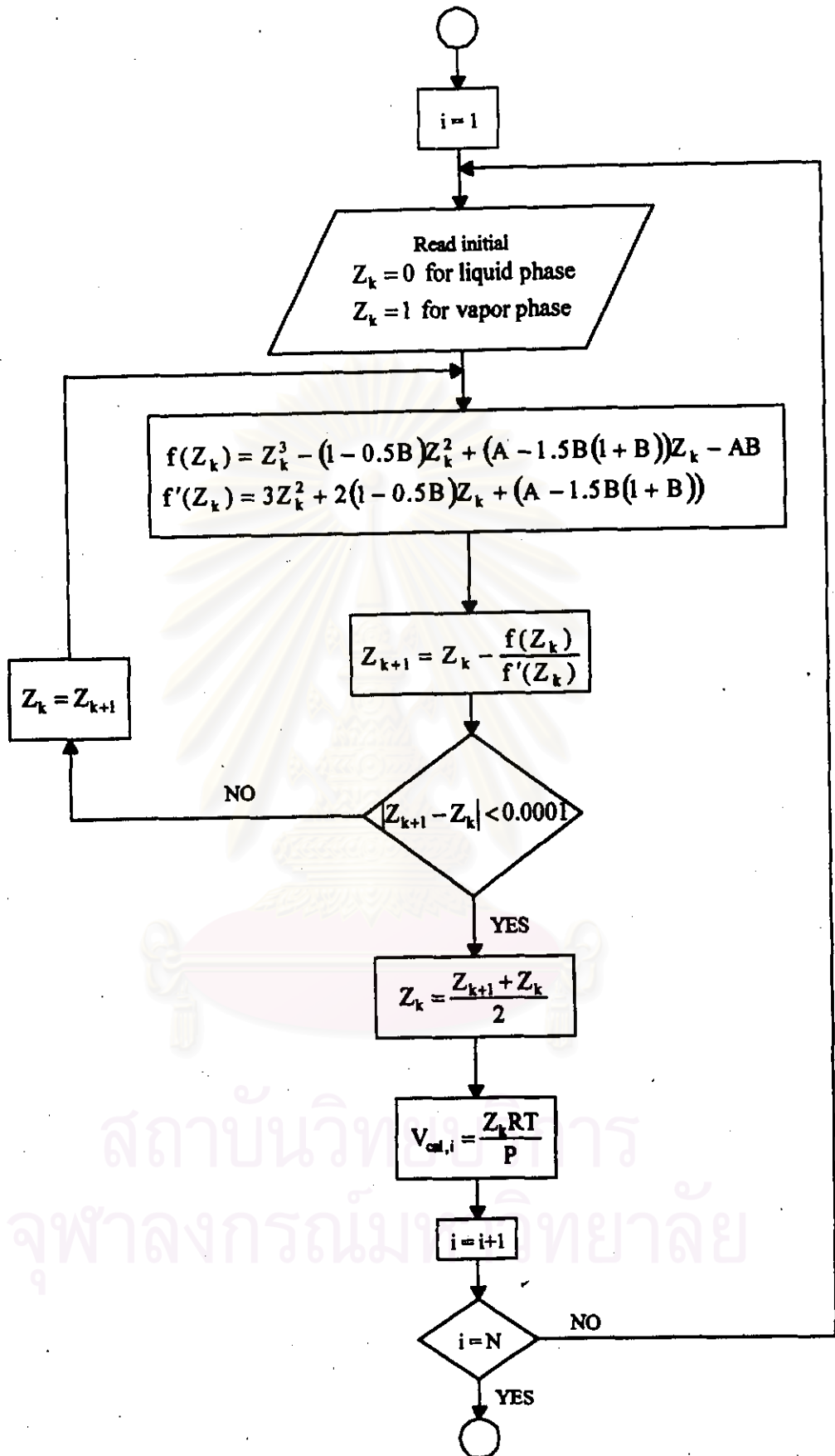


Figure 5.5 Flow chart of subprogram Func MRK.

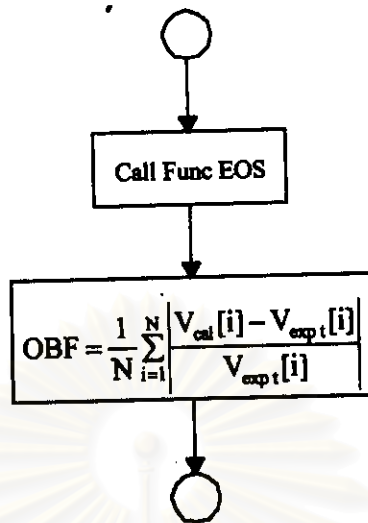


Figure 5.6 Flow chart of subprogram Func OBFN.

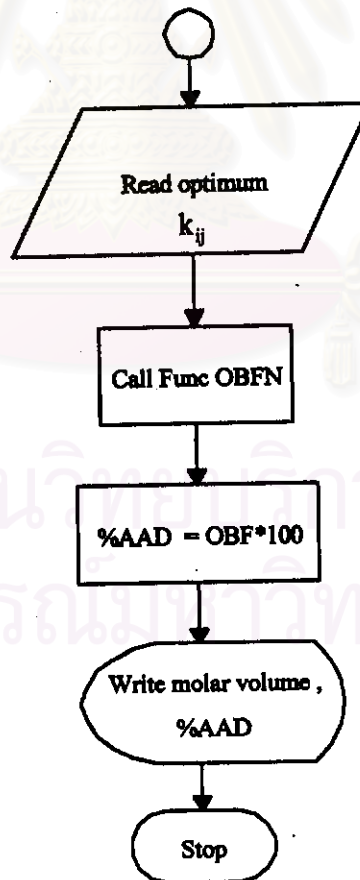


Figure 5.7 Flow chart of subprogram Func Volume.