

CHAPTER VII

VAPOR-LIQUID EQUILIBRIA

7.1 INTRODUCTION

Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. It means a balance of all potentials that may cause change. In engineering practice, the assumption of equilibrium is justified when it leads to results of satisfactory. For instance, in the each tray of a distillation column, equilibrium between vapor and liquid phases is assumed. Finite vaporization rates this is an approximation, but it does not introduce significant error into engineering calculation.

If a system containing fixed amounts of chemical species and consisting of liquid and vapor phases in intimate contact is completely isolated, then there is no tendency for any change in time to happen within the system. Pressure, temperature, and phase compositions reach final values which thereafter remain fixed. However, at the microscopic level, conditions are not static. Molecules in one phase at a given instance are not the same molecules as those in that phase at a latter time. Molecules with sufficiently high velocities near the interface boundary overcome surface forces and pass into the other phase. However, the average rate of passage of molecules is the same in both directions, and there is no net transfer of material between the phases.

7.2 VAPOR-LIQUID EQUILIBRIA FOR IDEAL SOLUTIONS

7.2.1 Ideal solutions

Solutions for which the fugacity of each component i (component of mixture) is equal to the mole fraction x_i times the fugacity of the pure component, f_i , at the same temperature and pressure as the solution are termed ideal solution.

$$\left(\bar{f}_i = x_i f_i\right)_{P,T} \quad (7-1)$$

This general expression defining an ideal solution reduces to the more common but less general forms for gases and liquids, Dalton's and Raoult's laws, respectively.

Dalton's law states that in a mixture of ideal gases each component exerts a pressure which depends on the total volume, temperature, and number of moles of component:

$$\bar{P}_i = \frac{n_i RT}{V} = \frac{n_i RT}{\bar{V} n_i} \quad (7-2)$$

$$\bar{P}_i = \frac{y_i RT}{\bar{V}} \quad (7-3)$$

where \bar{P}_i = partial pressure of i
 y_i = molar fraction of i in mixture
 V = total volume of mixture
 \bar{V} = molar volume of mixture
 n_i = number of moles for compound of i
 n_i = total number of moles for compound

Thus
$$P = \sum_i \bar{P}_i \quad (7-4)$$

where P = total pressure

Raoult's law for ideal-liquid solutions is a direct application equation (7-1), where the forces between identical molecules or unlike molecules can be assumed to be equal. This law is usually limited to mixtures of nearly adjacent compounds in homologous series, such as methanol and ethanol, n-pentane and n-heptane at low pressure. The low-pressure criterion allows the pure-component fugacity f_i to be replaced by pure-component vapor pressure P_i^{sat} such that

$$\bar{P}_i = x_i P_i^{sat} \quad (7-5)$$

$$P = \sum_i x_i P_i^{sat} \quad (7-6)$$

If a liquid solution is ideal, its vapor will be certainly ideal and Dalton's and Raoult's laws can be combined.

$$\bar{P}_i = x_i P_i^{sat} = y_i P \quad (7-7)$$

This relation is used to predict the vapor-liquid equilibria of ideal solutions. Ideal solutions, in general, assume no chemical interactions, similar molecular sizes, and equal attractive and repulsive forces between like and unlike molecules. Thus, a mixture of isomers, such as ortho-, meta-, and para-xylene, conforms very closely to ideal solutions. So do mixtures of adjacent members of a homologous series, as for example, n-hexane/n-heptane, ethanol/propanol, and benzene/toluene. Other examples are acetone/acetonitrile and acetonitrile/nitromethane.

7.2.2 Bubble point

Bubble point is a temperature or pressure at which a liquid of known composition first begin to boil.

Bubble-point pressure calculation

If we know x_k (mole fractions in liquid phase of component k) and T (temperature), and y_k (mole fractions in vapor phase of component k), P (pressure) will be calculated. Since Raoult's law gives

$$y_k P = x_k P_k^{sat} \quad (k = 1, 2, \dots, N) \quad (7-8)$$

$$P = \sum_k x_k P_k^{sat} \quad (7-9)$$

k = number of component

P is calculated by equation (7-9), while each y_k is found from Raoult's law and P^{sat} is calculated by Antoine equation. An algorithm of bubble point pressure calculation is expressed in Figure 7.1.

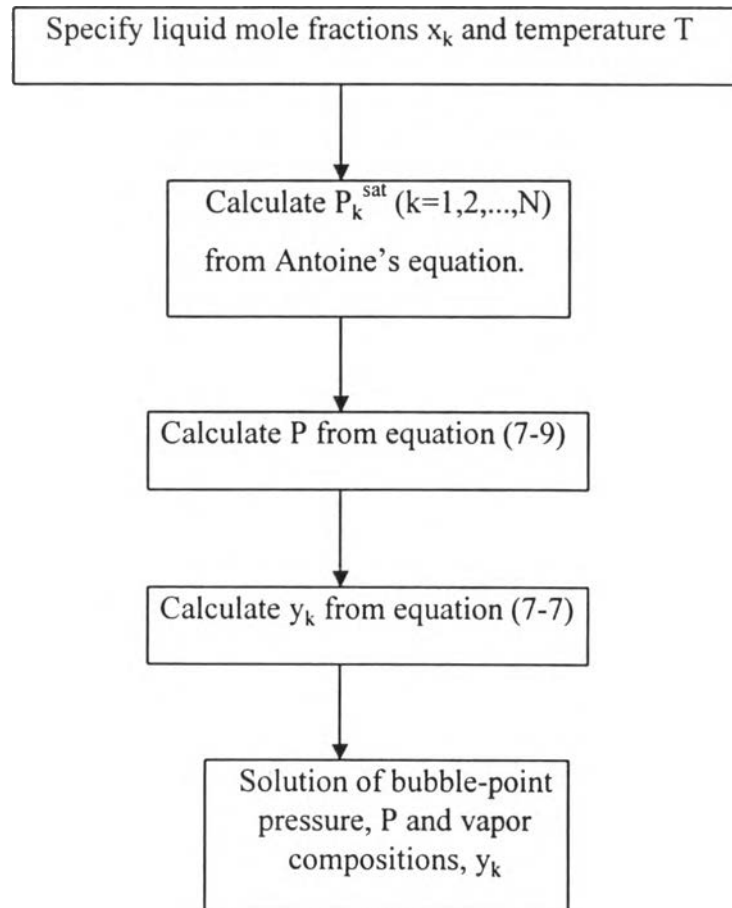


Figure 7.1 An algorithm for solving bubble-point pressure

Bubble-point temperature calculation

A bubble-point temperature calculation of y_k and T , can be carried out if x_k and P , is known.

$$P = P_i^{\text{sat}} \sum_k x_k \frac{P_k^{\text{sat}}}{P_i^{\text{sat}}} \quad (7-10)$$

where i is an arbitrarily selected member of set $\{k\}$. For example, ternary components system (methane, ethane, and propane), set $\{k\}$ equals to $\{\text{methane, ethane, and propane}\}$ and propane is an arbitrarily selected member of set $\{\text{methane, ethane, and propane}\}$. Solution for P_i^{sat} gives

$$P_i^{\text{sat}} = \frac{P}{\sum_k x_k \alpha_{ki}} \quad (7-11)$$

where

$$\alpha_{ki} = \frac{P_k^{\text{sat}}}{P_i^{\text{sat}}} \quad (7-12)$$

when the vapor pressures are given by Antoine equations,

$$\ln \alpha_{ki} = A_k - A_i - \frac{B_k}{T + C_k} + \frac{B_i}{T + C_i} \quad (7-13)$$

A, B, C are constants of Antoine equation.

An iterative procedure starts with solution of equation (7-13) with an initial value of T provided by the equation

$$T_0 = \sum_k x_k T_k^{\text{sat}} \quad (7-14)$$

Equation (7-11) then yields P_i^{sat} , and we get a new value of T from the Antoine equation

$$T = \frac{B_i}{A_i - \ln P_i^{\text{sat}}} - C_i \quad (7-15)$$

Calculation sequence is repeated until there is no significant changes in T . Final values of P_k^{sat} are found from Antoine equations, and final y_k values can be computed from Raoult's law. Figure 7.2 shown an algorithm of bubble-point temperature.

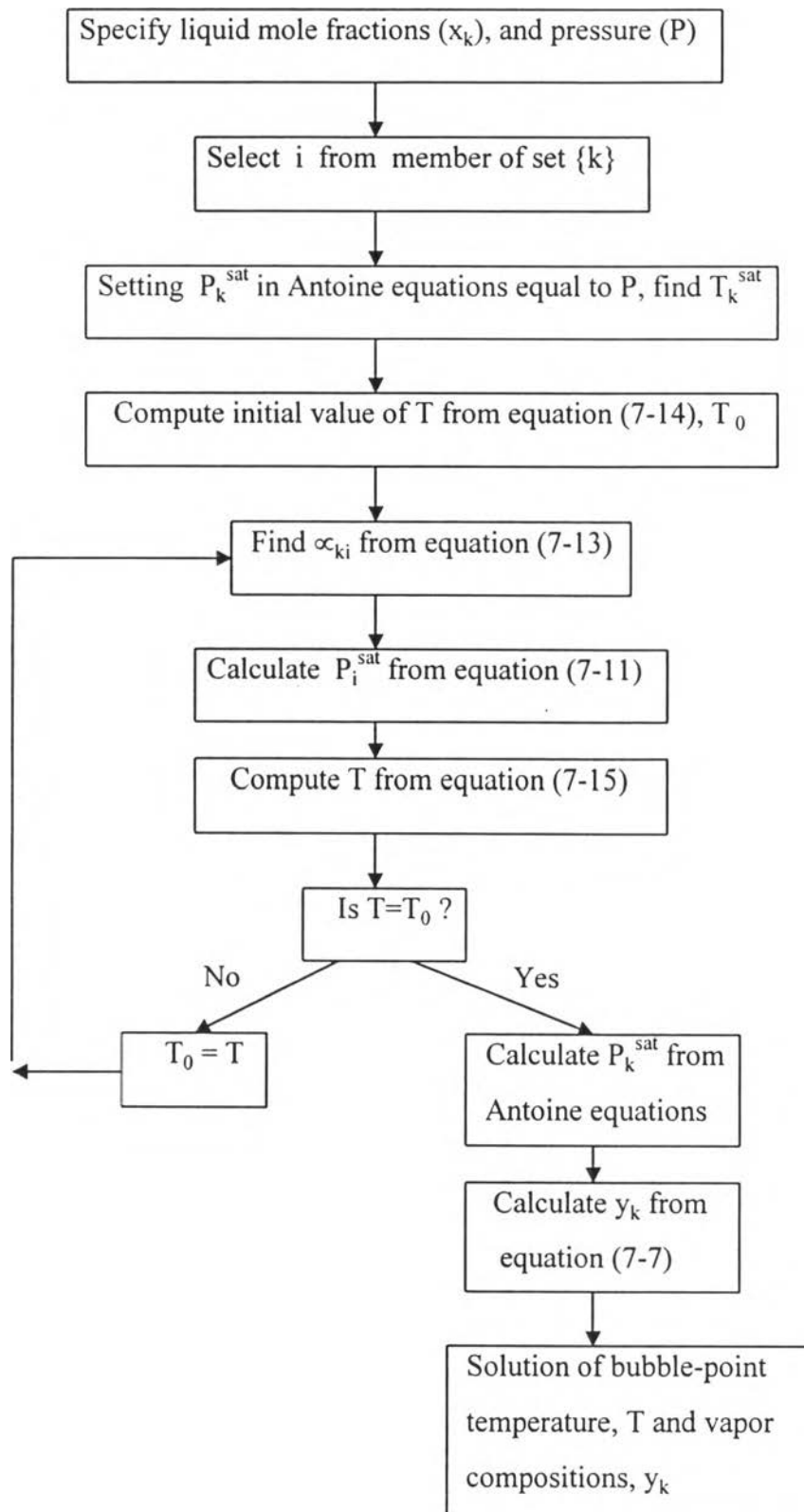


Figure 7.2 An algorithm for solving bubble-point temperature

Dew point

Dew point is a temperature and pressure at which of known composition first begins to condense.

Dew-point pressure calculation

If T , y_k are given, x_k and P will be computed.

$$x_k = \frac{y_k P}{P_k^{sat}} \quad (k=1,2,\dots,N) \quad (7-16)$$

$$1 = P \sum_k \frac{y_k}{P_k^{sat}} \quad (7-17)$$

$$P = \frac{1}{\sum_k (y_k / P_k^{sat})} \quad (7-18)$$

P is calculated by equation (7-18), each x_k is given by equation (7-16).

Figure 7.3 expresses an algorithm of dew-point pressure.

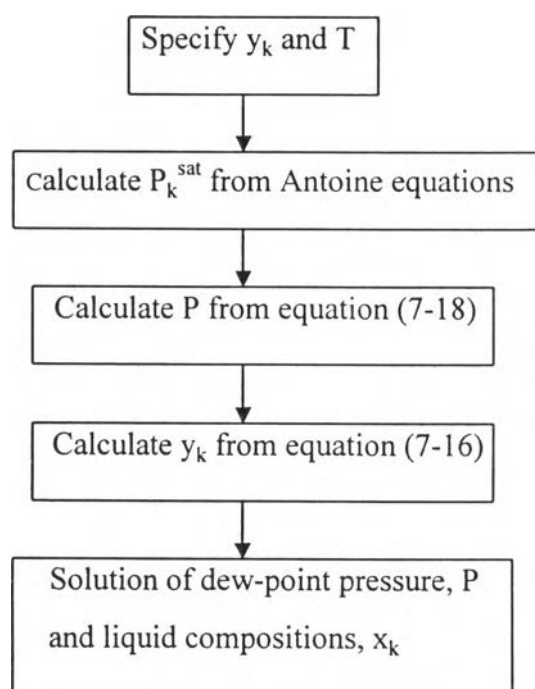


Figure 7.3 An algorithm for solving dew-point pressure.

Dew-point temperature calculation

In dew point-temperature calculation, we must know y_k and P and then seek x_k and T . We write equation (7-18) as

$$P = \frac{P_i^{sat}}{\sum_k y_k (P_i^{sat} / P_k^{sat})} \quad (7-19)$$

$$P_i^{sat} = P \sum_k (y_k / \alpha_{ki}) \quad (7-20)$$

An iterative process starts with equation (7-13), with an initial value

$$T_0 = \sum_k y_k T_k^{sat} \quad (7-21)$$

After iteration converges, we calculate the P_k^{sat} and the final x_k by equation (7-16). An algorithm for solving dew point temperature is shown in Figure 7.4.

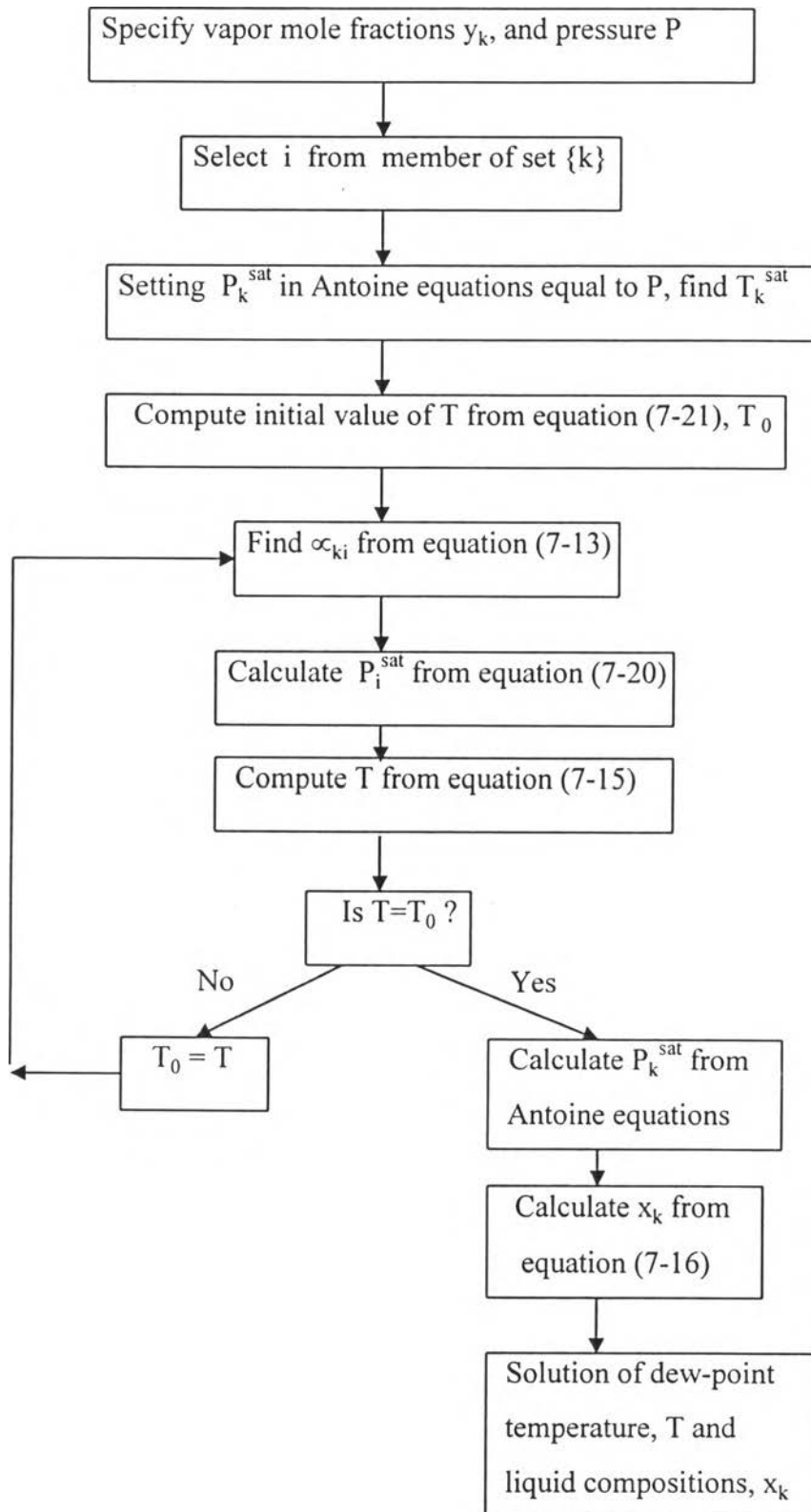


Figure 7.4 An algorithm for solving dew-point temperature

Isothermal flash calculation

Flash distillation is a process that occurs when a liquid under pressure passes through a valve to a pressure low enough that some of the liquid vaporizes. Flash distillation produces a two-phase stream of vapor and liquid in equilibrium. In isothermal flash distillation the quantities and compositions of the vapor and liquid phase which are making up a two phase system in equilibrium can be calculated when we know pressure, temperature, and overall compositions. Consider a system containing unit mole of chemical species, and having an overall composition represented by the set of mole fractions $\{z_i\}$. Let L be the moles of liquid, with mole fractions $\{x_i\}$, and let V be the moles of vapor, with mole fractions $\{y_i\}$. The material balance equations are

$$L + V = 1 \quad (7-22)$$

$$z_i = x_i L + y_i V \quad (i=1,2,\dots,N) \quad (7-23)$$

$$z_i = x_i(1 - V) + y_i V \quad (i=1,2,3,\dots,N) \quad (7-24)$$

We can write Raoult's law as

$$y_i = K_i x_i \quad (K_i \text{ is a K-value}) \quad (7-25)$$

$$K_i = \frac{P_i^{sat}}{P} \quad (7-26)$$

P_i^{sat} is a function of T only and, K_i is a function of T and P. Substituting $x_i=y_i/K_i$ in equation (7-24) gives

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (i = 1, 2, 3, \dots, N) \quad (7-27)$$

Since $\sum y_i = 1$, the sum of equation (7-27) gives

$$\sum_i \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \quad (7-28)$$

In the above equations, T, P, and $\{z_i\}$ are known but only V in equation (7-28) is unknown. Thus, V is solved by numerical method. The y_i are found from equation (7-27) and the x_i from equation (7-25). Isothermal flash calculation is expressed in Figure 7.5.

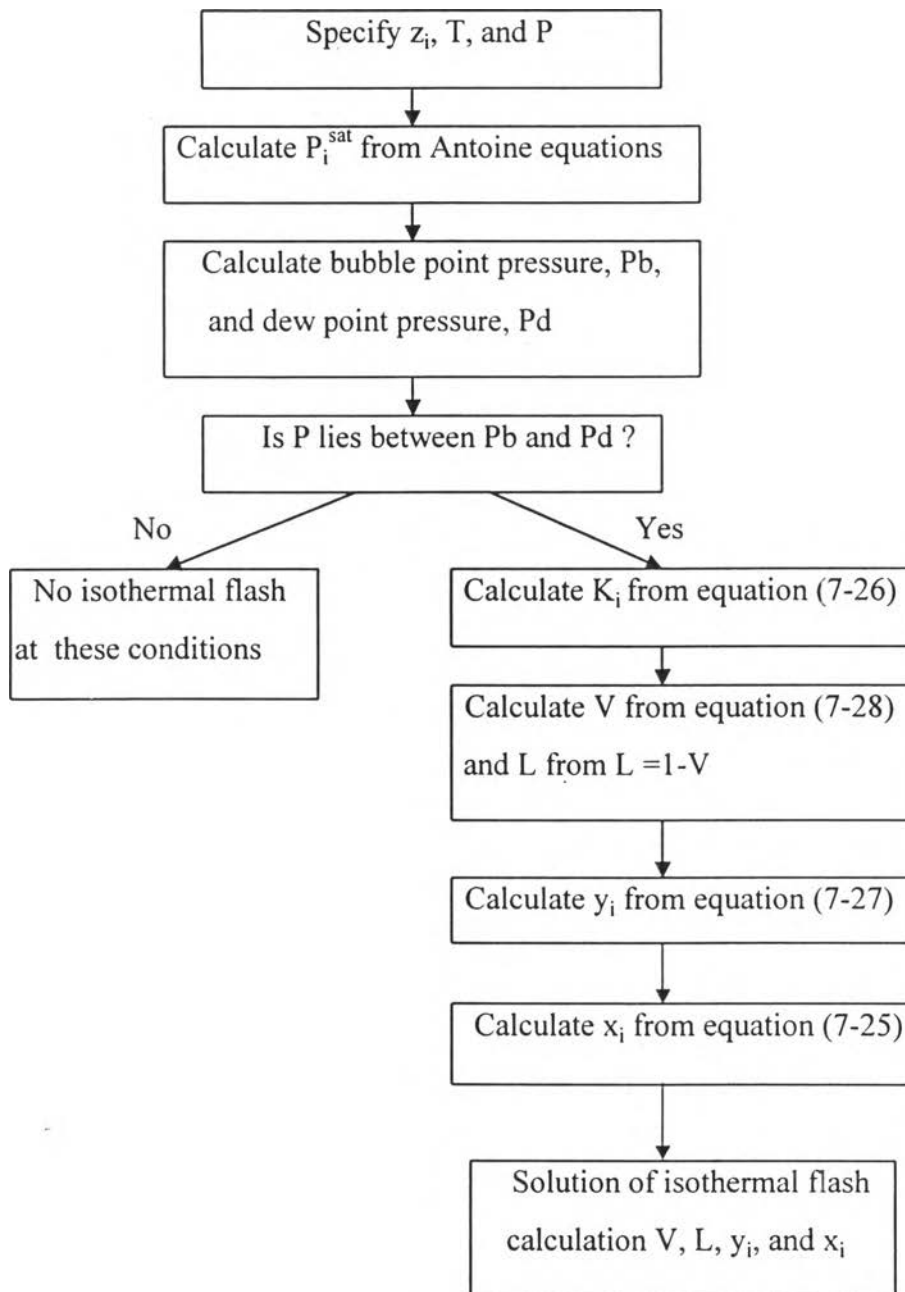


Figure 7.5 An algorithm of solving isothermal flash calculation.

7.3 VAPOR-LIQUID EQUILIBRIA FOR NONIDEAL SOLUTIONS

In the analysis of distillation and other vapor-liquid separations processes one must estimate the compositions of vapor and liquid mixtures in equilibrium. The starting point for all vapor-liquid calculations is the equilibrium criterion

$$\bar{f}_i^L(T, P, x_i) = \bar{f}_i^V(T, P, y_i) \quad (7-29)$$

\bar{f}_i = fugacity of a species in mixture

where the superscripts L and V refer to liquid and vapor phases, respectively. There are two models to calculate vapor-liquid equilibria for nonideal solutions one is equation of state and the other is activity coefficient. Different between two models are as follows:

1. Activity coefficient models can be used for liquid mixtures of all species. It is possible to represent highly non-ideal mixtures (mixtures that contain strong polarity or hydrogen bonded, polymers or electrolytes). However, the model will not give a good description of an expanded liquid near the vapor-liquid critical point.

2. Equation of state can be used for both gas and liquid phases. Good phase equilibrium predictions can be made over a wide range of temperatures and pressures, including near the critical region. Furthermore, not only can the compositions of coexisting phases be predicted from an equation of state, but also can other properties such as their densities and enthalpy. Equation of state are applicable to normal fluids (nitrogen, oxygen, carbonmonoxide, and hydrocarbons), carbondioxide, hydrogen, and slightly polar substance. It works even at high pressures. The disadvantage of equation of state is that it can not deal with number of situations which coincide with the cases where the Corresponding States Theory also does not apply, namely dealing with polar compounds, large molecules (polymers), and electrolytes.

In this work, equation of state is taken into consideration because it is advantageous over the use of activity coefficients as follows:

1. Continuity in the critical region is assured (although convergence may be hard to achieve).

2. A wide variety of properties can be derived from equation of state such as compressibility factor, density (inverse of the specific volume), and departure functions.

7.4 VAPOR-LIQUID EQUILIBRIA USING EQUATIONS OF STATE(EOS)

For high pressure, equation of state is appropriate for calculating phase equilibrium. The starting point for any phase equilibrium calculation is the equality of fugacities of each species in each phase.

$$\bar{f}_i^L(T, P, x_i) = \bar{f}_i^V(T, P, y_i) \quad (7-29)$$

An equation of state will be used to calculate species fugacities in both phases. Phase equilibrium calculations with equation of state are iterative but not too complicated to be done on a computer.

Bubble-point pressure calculation

In calculation of bubble-point pressure, the compositions of liquid (x_i), and temperature(T) must be known. One would need to make an initial guess for the bubble-point pressure (P_b) and the vapor fractions (or, perhaps more easily, for the values of $K_i = y_i / x_i$), and then check to see if $\sum y_i = 1$ and the equality of species fugacities (equation (7-29)) is satisfied for each species. If these restrictions are not satisfied, the pressure and K_i values must be adjusted and the calculation must be repeated.

The initial guess for bubble-point pressure and for K_i values for all species in the mixture do not affect the final solution. It may influence the number of iterations required to obtain the solution.

One possible set of initial guesses is obtained by assuming ideal liquid and vapor mixtures, that is

$$Pb = \sum x_i P_i^{sat} \quad (7-30)$$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{Pb} \quad (7-31)$$

where the pure component vapor pressure can be estimated by using the equation of state. An algorithm for solving bubble-point pressure is shown in Figure 7.6.

Dew-point pressure calculation

Calculation of dew-point pressure, we know the composition of vapor (y_i) and temperature. We must calculate dew-point pressure (Pd) and liquid mole fractions. Set of initial guesses is as follows:

$$Pd = \sum y_i P_i^{sat} \quad (7-32)$$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{Pb} \quad (7-31)$$

The procedure to calculate dew-point pressure is the same as bubble-point pressure calculation. A flow diagram for an algorithm for solving dew-point pressure is expressed in figure 7.7.

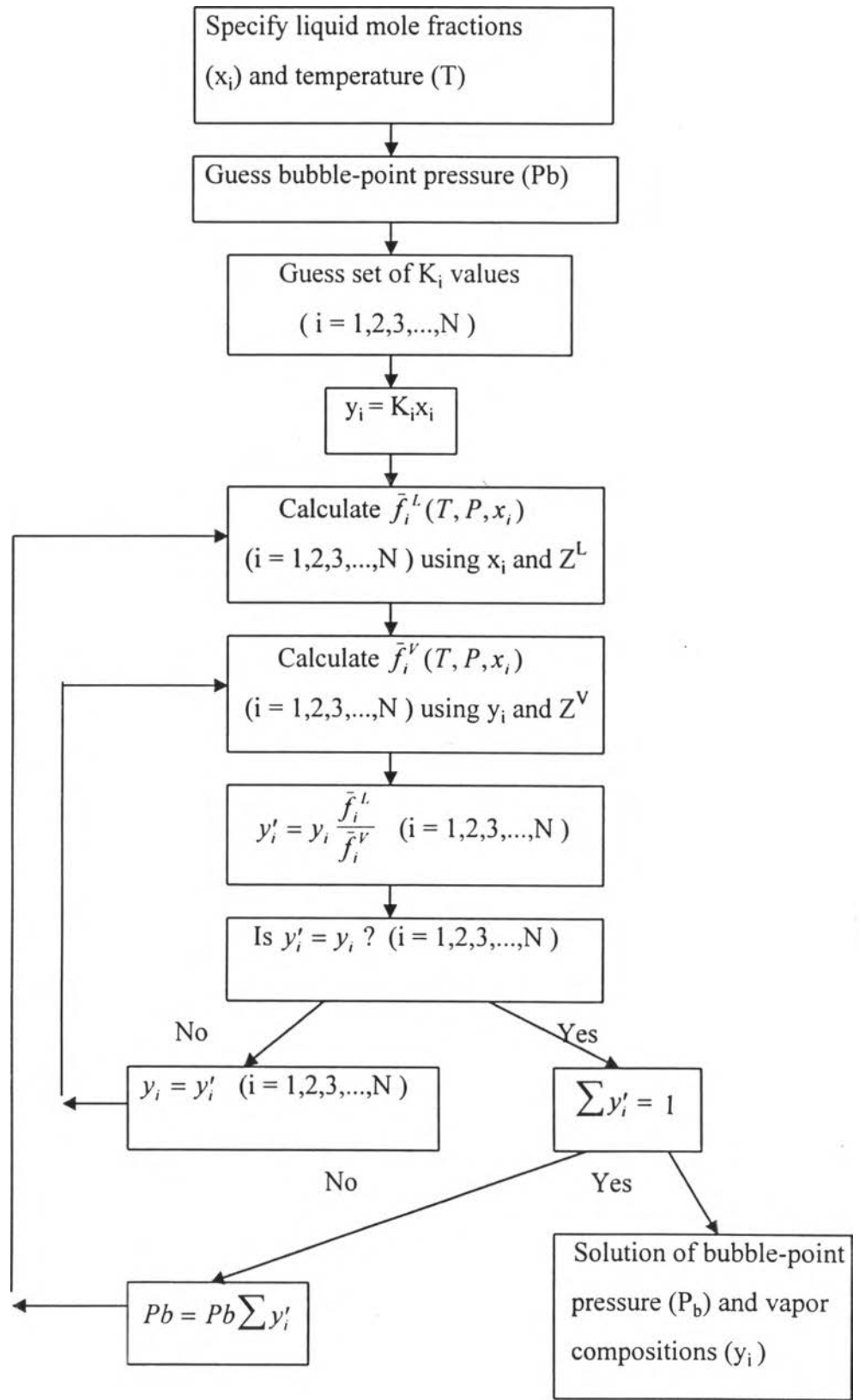


Figure 7.6 An algorithm for solving the bubble-point pressure using equation of state

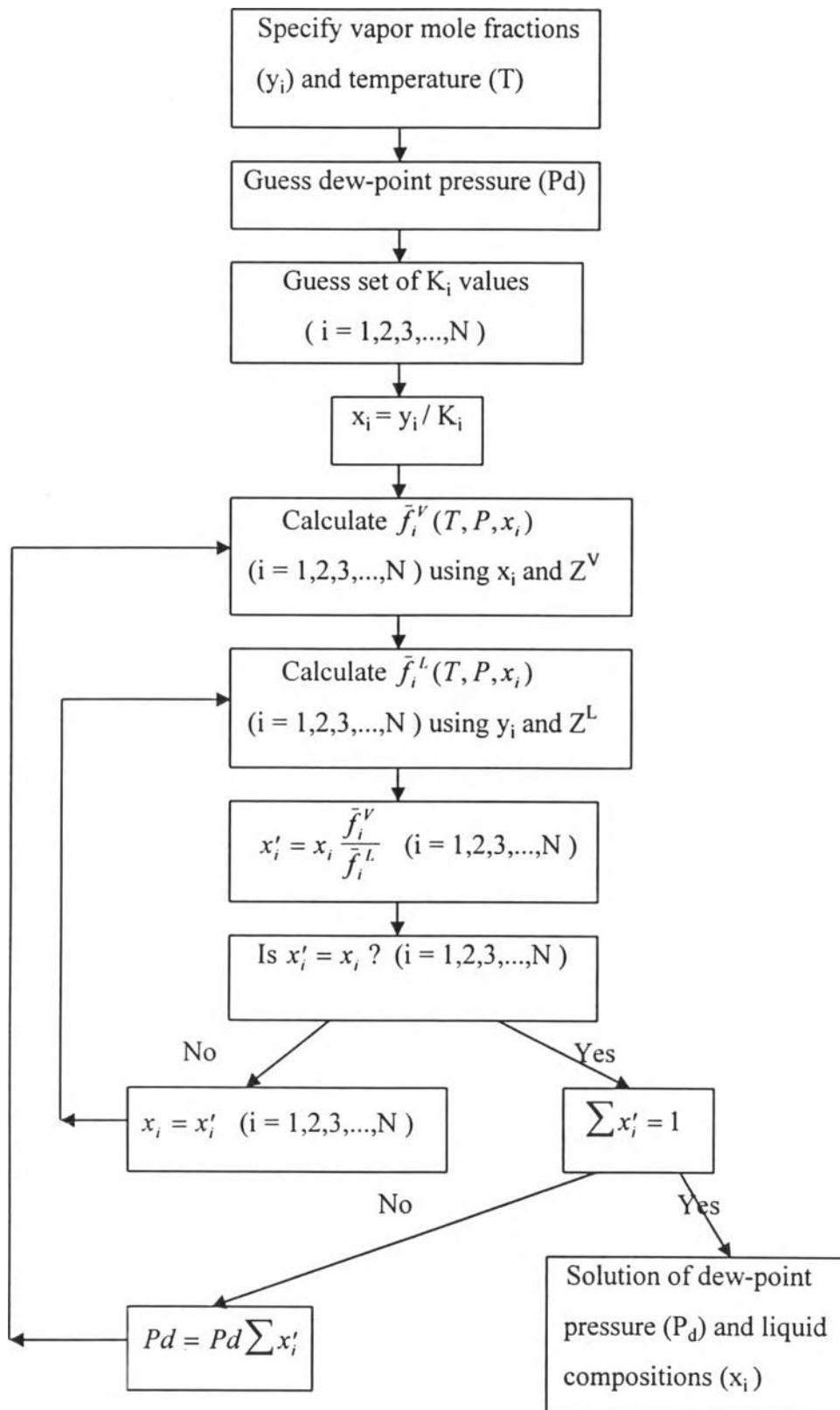


Figure 7.7 An algorithm for solving the dew-point pressure using equation of state

Bubble-point temperature calculation

Calculation of bubble-point temperature (T_b) is slightly change from bubble-point pressure calculation. We must determine liquid mole fractions, pressure and replace $P_b = P_b \sum y'_i$, with $T_b = T_b / \sum y'_i$. Set of initial guesses is as follows:

$$T_b = \sum x_i T_{b,i} \quad (7-33)$$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P_b} \quad (7-31)$$

An algorithm for solving bubble-point temperature using equation of state is expressed in Figure 7.8.

Dew-point temperature calculation

Calculation of dew-point temperature, we specify vapor mole fractions and pressure. Dew-point temperature (T_d) and liquid mole fractions will be obtained from iteration. Set of initial guesses is as follows:

$$T_d = \sum y_i T_{d,i} \quad (7-34)$$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P_b} \quad (7-31)$$

A flow diagram of an algorithm for solving dew-point temperature is expressed in Figure 7.9.

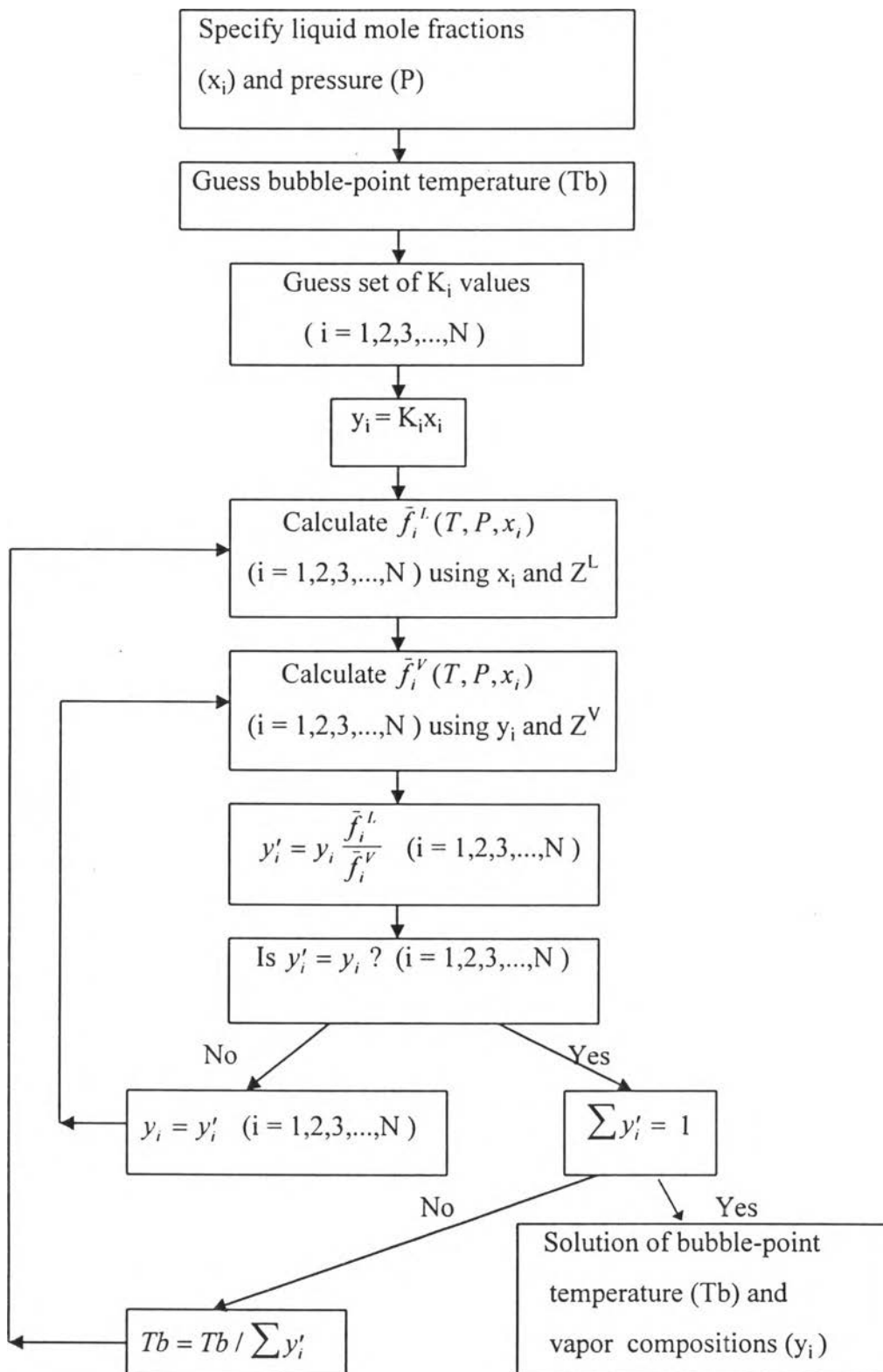


Figure 7.8 An algorithm for solving the bubble-point temperature using equation of state

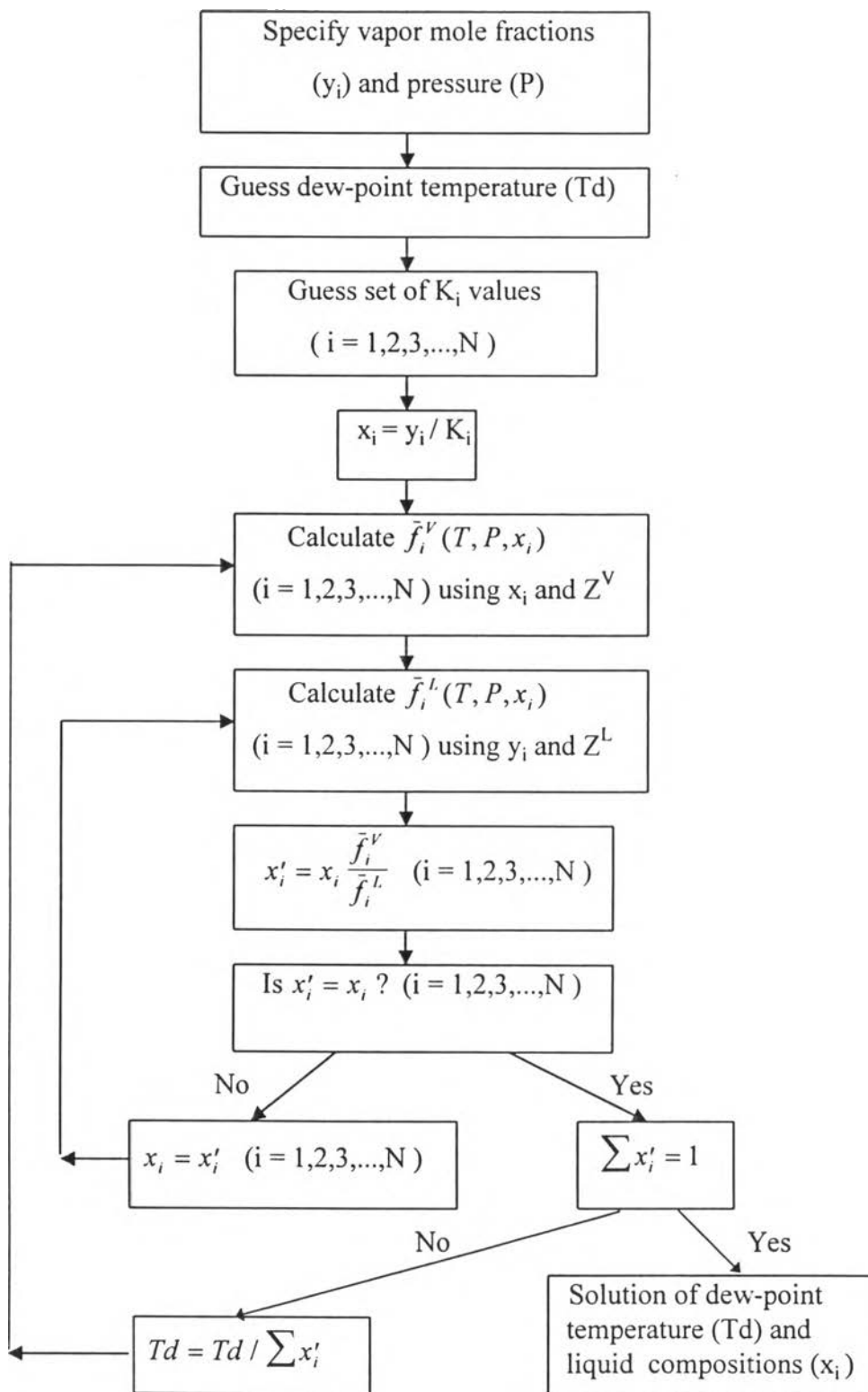


Figure 7.9 An algorithm for solving the dew-point temperature using equation of state

Isothermal flash calculation

Isothermal flash calculation, the equality of species fugacities relation (equation (7-29)) and the mass balances which is based on 1 mole of feed of mole fractions z_i must be satisfied, that is

$$x_i L + y_i V = z_i \quad (i = 1, 2, 3, \dots, N) \quad (7-35)$$

$$L + V = 1 \quad (7-36)$$

The summation conditions are

$$\sum x_i = 1 \quad \text{and} \quad \sum y_i = 1 \quad (7-37)$$

For isothermal flash calculation, temperature and pressure are known but liquid mole fractions, vapor mole fractions and liquid-to-vapor split (L/V) are unknown. Set of initial guesses of isothermal flash calculation is as follows:

$$x_i = \frac{z_i}{L + K_i(1 - L)} \quad (7-38)$$

$$y_i = K_i x_i \quad (7-39)$$

Furthermore, from equation (7-37), we have

$$\sum_{i=1} x_i = \sum \frac{z_i}{L + K_i(1 - L)} = 1 \quad (7-40)$$

$$\sum_{i=1} y_i = \sum \frac{K_i z_i}{L + K_i(1 - L)} = 1 \quad (7-41)$$

or, equivalently,

$$\sum x_i - \sum y_i = \sum \frac{(1 - K_i) z_i}{L + K_i(1 - L)} = 0 \quad (7-42)$$

An algorithm for isothermal flash calculation is shown in Figure 7.10.

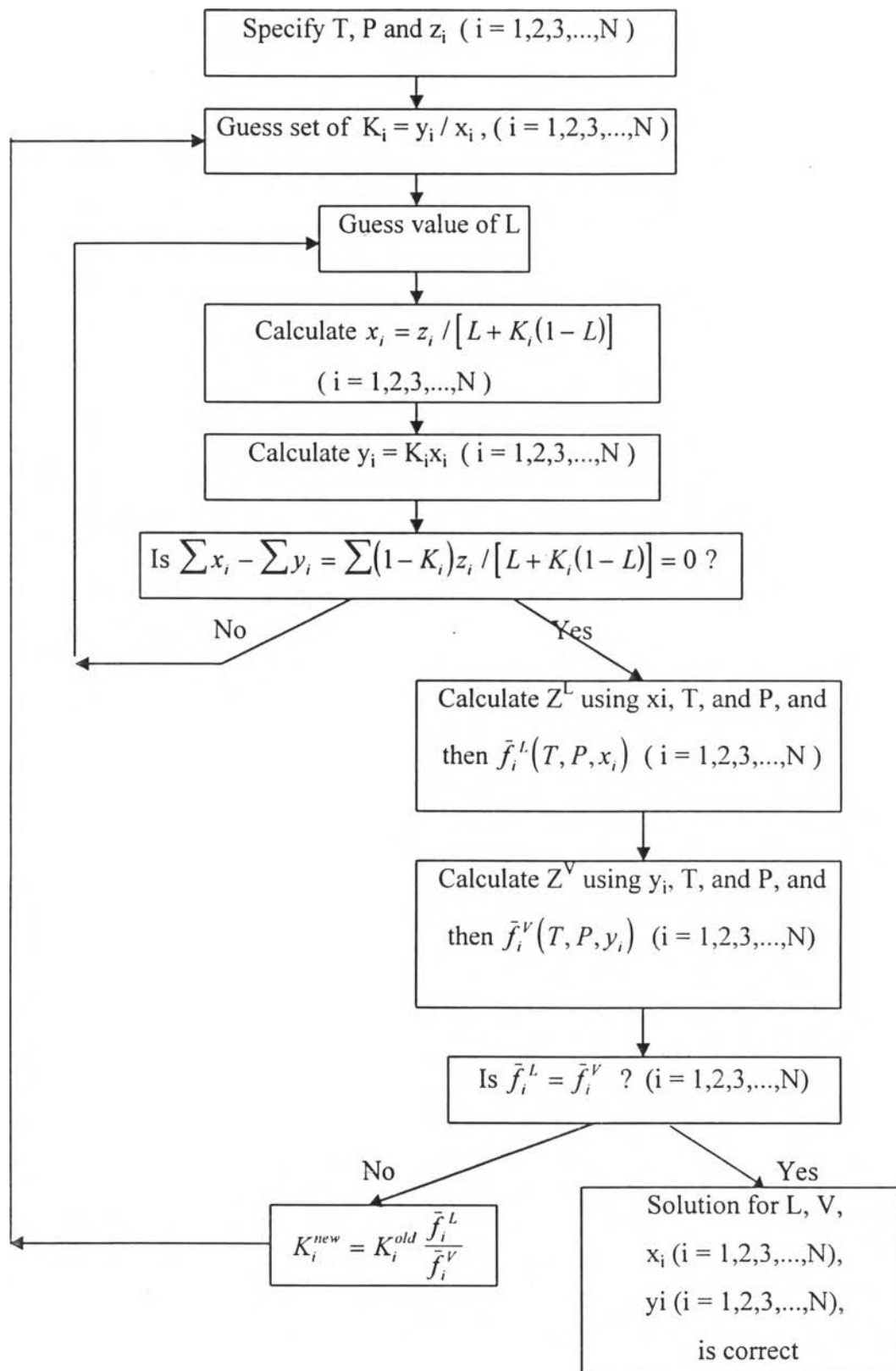


Figure 7.10 An algorithm for solving isothermal flash using equation of state