

Figure 14.1: Block diagram for the calculation *BUBL P*.

to unity, the set is normalized by setting $x_i = x_i / \sum_i x_i$. Subsequent recalculation of P by Eq. (14.11) leads to the outer loop and iteration to convergence on final values for P and $\{x_i\}$.

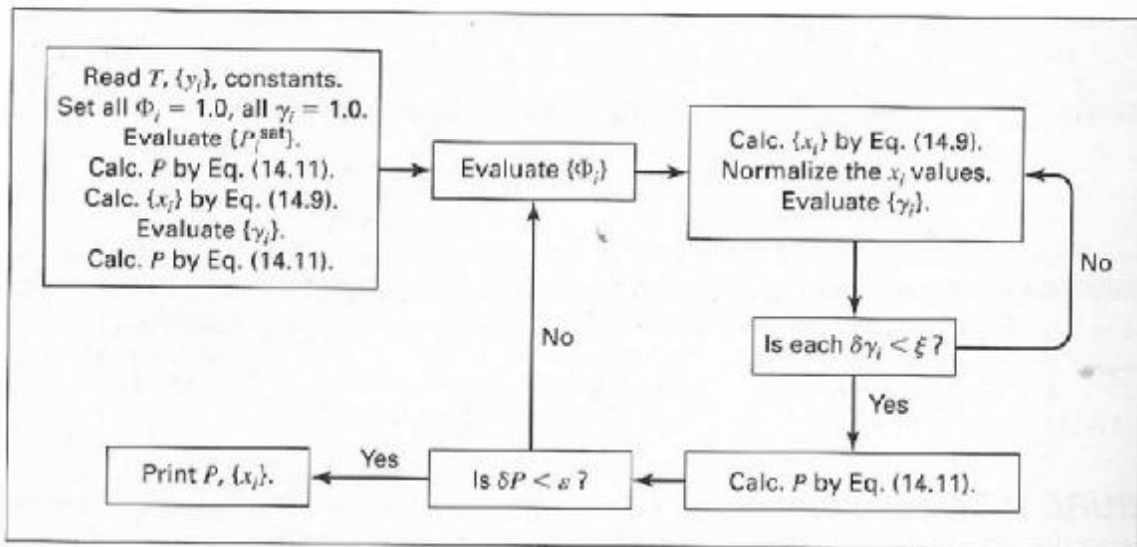


Figure 14.2: Block diagram for the calculation *DEW P*.

In *BUBL P* and *DEW P* calculations, temperature is given, allowing immediate and final calculation of $\{P_i^{\text{sat}}\}$. This is not the case for procedures *BUBL T* and *DEW T*, where the temperature is unknown. Because iteration is controlled by T , an initial estimate is required. Depending on whether $\{x_i\}$ or $\{y_i\}$ is known, it is given by:

$$T = \sum_i x_i T_i^{\text{sat}} \quad \text{or} \quad T = \sum_i y_i T_i^{\text{sat}}$$

where

$$T_i^{\text{sat}} = \frac{B_i}{A_i - \ln P} - C_i \quad (14.12)$$

Although individual vapor pressures are strong functions of temperature, vapor-pressure ratios are not, and calculations are facilitated by their introduction. Multiplying the right sides of Eqs. (14.10) and (14.11) by P_j^{sat} (outside the summation), dividing by P_j^{sat} (inside the summation), and solving for the P_j^{sat} appearing outside the summation gives the two results:

$$P_j^{\text{sat}} = \frac{P}{\sum_i (x_i \gamma_i / \Phi_i) (P_i^{\text{sat}} / P_j^{\text{sat}})} \quad (14.13)$$

$$P_j^{\text{sat}} = P \sum_i \frac{y_i \Phi_i}{\gamma_i} \left(\frac{P_j^{\text{sat}}}{P_i^{\text{sat}}} \right) \quad (14.14)$$

The summations are over all species including j , which is an *arbitrarily selected species*. Once P_j^{sat} is known, the corresponding value of T is found from Eq. (14.3), written:

$$T = \frac{B_j}{A_j - \ln P_j^{\text{sat}}} - C_j \quad (14.15)$$

BUBL T Calculations: Figure 14.3 shows an iterative scheme with input, P , $\{x_i\}$, and parameters. In the absence of T and $\{y_i\}$ values, set $\Phi_i = 1$. The simple iteration scheme that follows is clear from the figure.

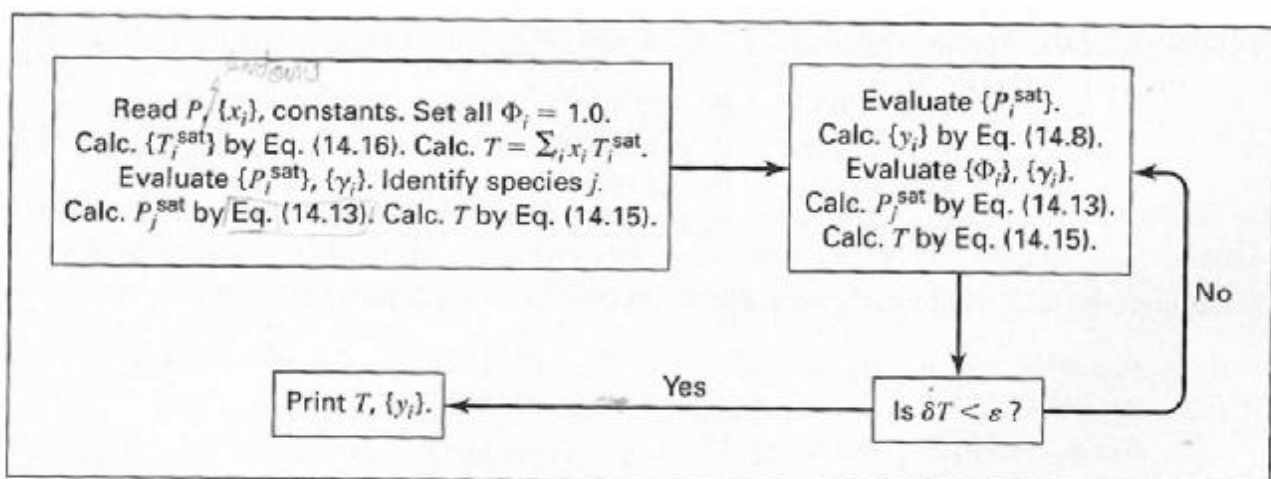
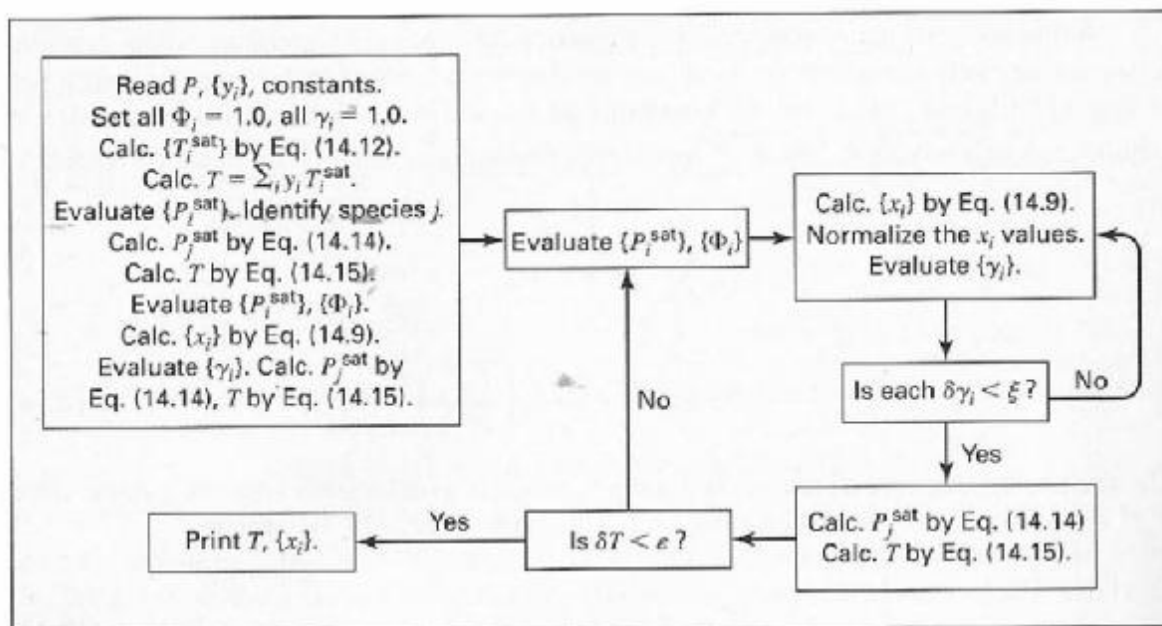


Figure 14.3: Block diagram for the calculation *BUBL T*.

DEW T Calculations: Here, neither T nor $\{x_i\}$ is known. The iteration scheme is shown in detail by Fig. 14.4. As in the *DEW P* procedure, the set $\{x_i\}$ calculated within the inner loop is not constrained to sum to unity, and is therefore normalized by setting $x_i = x_i / \sum_i x_i$.

Dewpoint and bubblepoint calculations are readily made with software packages such as Mathcad[®] and Maple[®], in which iteration is an integral part of an equation-solving routine. Calculations for multicomponent systems made either with the iteration schemes detailed here or with software packages are readily carried out by computer.

Figure 14.4: Block diagram for the calculation DEW T .

The results for a complete *BUBL T* calculation are shown in Table 14.1 for the system *n*-hexane(1)/ethanol(2)/methylcyclopentane(3)/benzene(4). The given pressure P is 1(atm), and the given liquid-phase mole fractions x_i are listed in the second column of Table 14.1. Parameters for the Antoine equations¹ [T in kelvins, P in (atm)], supplied as input data, are:

$$\begin{array}{lll}
 A_1 = 9.2033 & B_1 = 2,697.55 & C_1 = -48.78 \\
 A_2 = 12.2786 & B_2 = 3,803.98 & C_2 = -41.68 \\
 A_3 = 9.1690 & B_3 = 2,731.00 & C_3 = -47.11 \\
 A_4 = 9.2675 & B_4 = 2,788.51 & C_4 = -52.36
 \end{array}$$

In addition, the following virial coefficients² (in $\text{cm}^3 \text{mol}^{-1}$) are provided:

$$\begin{array}{llll}
 B_{11} = -1,360.1 & B_{12} = -657.0 & B_{13} = -1,274.2 & B_{14} = -1,218.8 \\
 B_{22} = -1,174.7 & B_{23} = -621.8 & B_{24} = -589.7 & \\
 B_{33} = -1,191.9 & B_{34} = -1,137.9 & & \\
 B_{44} = -1,086.9 & & &
 \end{array}$$

Finally, input information includes parameters for the UNIFAC method (App. H). The calculated values of T and the vapor-phase mole fractions y_i compare favorably with experimental values.³ Also listed in Table 14.1 are final computed values of P_i^{sat} , Φ_i , and γ_i .

¹R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3d ed., app. A, McGraw-Hill, New York, 1977.

²From the correlation of J. G. Hayden and J. P. O'Connell, *Ind. Eng. Chem. Proc. Des. Dev.*, vol. 14, pp. 289-291, 1975.

³J. E. Sinor and J. H. Weber, *J. Chem. Eng. Data*, vol. 5, pp. 243-247, 1960.