

Therefore, water condenses first when the temperature reaches 211°F. This is the dew-point temperature of the mixture at the system pressure. As the temperature is further reduced, the number of moles of water in the vapor decreases, causing the partial pressure of water to decrease below 14.5 psia and the partial pressure of nC_8 to increase above 4.8 psia. Thus, nC_8 begins to condense, forming a second liquid at a temperature higher than 194°F but lower than 211°F. This temperature, referred to as the *secondary dew point*, must be determined iteratively. The calculation is simplified if the bubble point of the mixture is computed first.

From (4-34),

$$P = 19.34 \text{ psi} = P_{H_2O}^s + P_{nC_8}^s \quad (1)$$

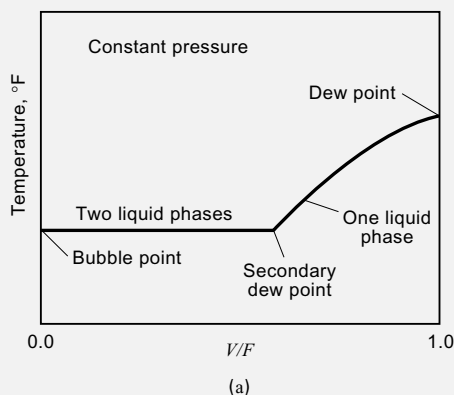
Thus, a temperature that satisfies (4-17) is sought:

$T, ^\circ\text{F}$	$P_{H_2O}^s, \text{psia}$	$P_{nC_8}^s, \text{psia}$	P, psia
194	10.17	4.8	14.97
202	12.01	5.6	17.61
206	13.03	6.1	19.13
207	13.30	6.2	19.50

By interpolation, $T = 206.7^\circ\text{F}$ for $P = 19.34 \text{ psia}$. Below 206.7°F the vapor phase disappears and only two immiscible liquids exist.

To determine the temperature at which one of the liquid phases disappears (the same condition as when the second liquid phase begins to appear, i.e., the secondary dew point), it is noted for this case, with only pure water and a pure HC present, that vaporization starting from the bubble point is at a constant temperature until one of the two liquid phases is completely vaporized. Thus, the secondary dew-point temperature is the same as the bubble-point temperature, or 206.7°F . At the secondary dew point, partial pressures are $p_{H_2O} = 13.20 \text{ psia}$ and $p_{nC_8} = 6.14 \text{ psia}$, with all of the nC_8 in the vapor. Therefore,

Component	Vapor		H ₂ O-Rich Liquid
	kmol	y	kmol
H ₂ O	53.9	0.683	21.1
nC_8	25.0	0.317	0.0
	78.9	1.000	21.1



If desired, additional flash calculations can be made for conditions between the dew point and the secondary dew point. The resulting flash curve is shown in Figure 4.31a. If more than one HC species is present, the liquid HC phase does not evaporate at a constant composition and the secondary dew-point temperature is higher than the bubble-point temperature. Then the flash is described by Figure 4.31b.

§4.10.3 Rigorous Method for a Vapor–Liquid–Liquid System

The rigorous method for treating a vapor–liquid–liquid system at a given temperature and pressure is called a *three-phase isothermal flash*. As first presented by Henley and Rosen [17], it is analogous to the isothermal two-phase flash algorithm in §4.4. The system is shown in Figure 4.32. The usual material balances and phase-equilibrium relations apply for each component:

$$Fz_i = Vy_i + L^{(1)}x_i^{(1)} + L^{(2)}x_i^{(2)} \quad (4-37)$$

$$K_i^{(1)} = y_i/x_i^{(1)} \quad (4-38)$$

$$K_i^{(2)} = y_i/x_i^{(2)} \quad (4-39)$$

A relation that can be substituted for (4-38) or (4-39) is

$$K_{D_i} = x_i^{(1)}/x_i^{(2)} \quad (4-40)$$

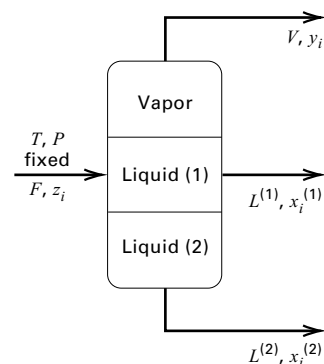


Figure 4.32 Conditions for a three-phase isothermal flash.

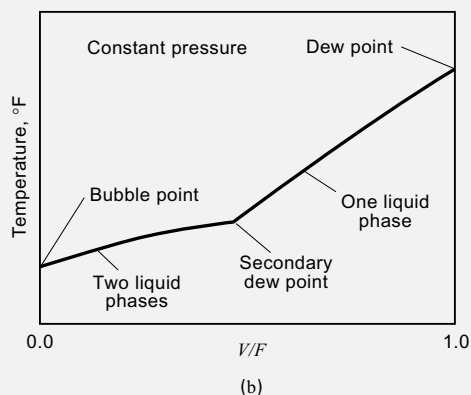


Figure 4.31 Typical flash curves for immiscible liquid mixtures of water and hydrocarbons at constant pressure: (a) only one hydrocarbon species present; (b) more than one hydrocarbon species present.

These equations are solved by a modification of the Rachford–Rice procedure if we let $\Psi = V/F$ and $\xi = L^{(1)}/(L^{(1)} + L^{(2)})$, where $0 \leq \Psi \leq 1$ and $0 \leq \xi \leq 1$. By combining (4-37), (4-38), and (4-39) with

$$\sum x_i^{(1)} - \sum y_i = 0 \quad (4-41)$$

and
$$\sum x_i^{(1)} - \sum x_i^{(2)} = 0 \quad (4-42)$$

to eliminate y_i , $x_i^{(1)}$, and $x_i^{(2)}$, two simultaneous equations in Ψ and ξ are obtained:

$$\sum_i \frac{z_i(1 - K_i^{(1)})}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi)K_i^{(1)}/K_i^{(2)} + \Psi K_i^{(1)}} = 0 \quad (4-43)$$

and

$$\sum_i \frac{z_i(1 - K_i^{(1)}/K_i^{(2)})}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi)K_i^{(1)}/K_i^{(2)} + \Psi K_i^{(1)}} = 0 \quad (4-44)$$

Values of Ψ and ξ are computed by solving nonlinear equations (4-43) and (4-44) simultaneously. Then the phase amounts and compositions are determined from

$$V = \Psi F \quad (4-45)$$

$$L^{(1)} = \xi(F - V) \quad (4-46)$$

$$L^{(2)} = F - V - L^{(1)} \quad (4-47)$$

$$y_i = \frac{z_i}{\xi(1 - \Psi)/K_i^{(1)} + (1 - \Psi)(1 - \xi)/K_i^{(2)} + \Psi} \quad (4-48)$$

$$x_i^{(1)} = \frac{z_i}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi)(K_i^{(1)}/K_i^{(2)}) + \Psi K_i^{(1)}} \quad (4-49)$$

$$x_i^{(2)} = \frac{z_i}{\xi(1 - \Psi)(K_i^{(2)}/K_i^{(1)}) + (1 - \Psi)(1 - \xi) + \Psi K_i^{(2)}} \quad (4-50)$$

Calculations for a three-phase flash are difficult because of the strong dependency of K -values on liquid-phase compositions when two immiscible liquids are present. This dependency appears in the liquid-phase activity coefficients (e.g., Eq. (4) in Table 2.3). In addition, it is not obvious how many phases will be present. A typical algorithm for determining phase conditions is shown in Figure 4.33. Calculations are best made with a process simulator, which can also perform adiabatic or nonadiabatic three-phase flashes by iterating on temperature until the enthalpy balance,

$$h_F F + Q = h_V V + h_{L^{(1)}} L^{(1)} + h_{L^{(2)}} L^{(2)} = 0 \quad (4-51)$$

is satisfied.

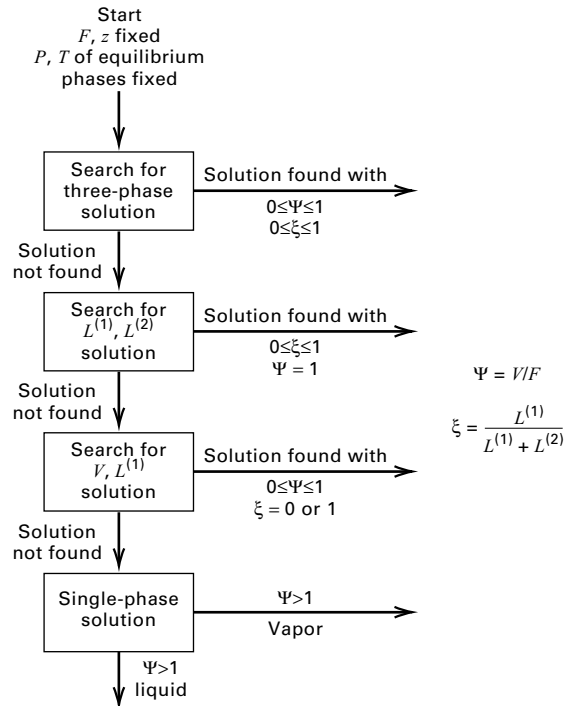


Figure 4.33 Algorithm for an isothermal three-phase flash.

EXAMPLE 4.19 Three-Phase Isothermal Flash.

In a process for producing styrene from toluene and methanol, the gaseous reactor effluent is as follows:

Component	kmol/h
Hydrogen	350
Methanol	107
Water	491
Toluene	107
Ethylbenzene	141
Styrene	350

If this stream is brought to equilibrium at 38°C and 300 kPa. Compute the amounts and compositions of the phases present.

Solution

Because water, hydrocarbons, an alcohol, and a light gas are present, the possibility of a vapor and two liquid phases exists, with methanol distributed among all phases. The isothermal three-phase flash module of the CHEMCAD process simulator was used with Henry's law for H_2 and UNIFAC for activity coefficients for the other components, to obtain:

Component	kmol/h		
	V	$L^{(1)}$	$L^{(2)}$
Hydrogen	349.96	0.02	0.02
Methanol	9.54	14.28	83.18
Water	7.25	8.12	475.63
Toluene	1.50	105.44	0.06
Ethylbenzene	0.76	140.20	0.04
Styrene	1.22	348.64	0.14
Totals	370.23	616.70	559.07

As expected, little H_2 is dissolved in either liquid. The water-rich liquid phase, $L^{(2)}$, contains little of the hydrocarbons, but much methanol. The organic-rich phase, $L^{(1)}$, contains most of the hydrocarbons and small amounts of water and methanol. Additional calculations at 300 kPa indicate that the organic phase condenses first, with a dew point = 143°C and a secondary dew point = 106°C.

SUMMARY

1. The Gibbs phase rule applies to intensive variables at equilibrium. It determines the number of independent variables that can be specified. This rule can be extended to determine the degrees of freedom (number of allowable specifications) for flow systems, including extensive variables. The intensive and extensive variables are related by material- and energy-balance equations and phase-equilibria data.
2. Vapor–liquid equilibrium conditions for binary systems can be represented by T – y – x , y – x , and P – x diagrams. Relative volatility for a binary system tends to 1.0 as the critical point is approached.
3. Minimum- or maximum-boiling azeotropes formed by nonideal liquid mixtures are represented by the same types of diagrams used for nonazeotropic (zeotropic) binary mixtures. Highly nonideal liquid mixtures can form heterogeneous azeotropes having two liquid phases.
4. For multicomponent mixtures, vapor–liquid equilibrium-phase compositions and amounts can be determined by isothermal-flash, adiabatic-flash, and bubble- and dew-point calculations. For non-ideal mixtures, process simulators should be used.
5. Liquid–liquid equilibrium conditions for ternary mixtures are best determined graphically from triangular and other equilibrium diagrams, unless only one of the three components (the solute) is soluble in the two liquid phases. In that case, the conditions can be readily determined algebraically using phase-distribution ratios (partition coefficients) for the solute.
6. Liquid–liquid equilibrium conditions for multi-component mixtures of four or more components are best determined with process simulators, particularly when the system is not dilute in the solute(s).
7. Solid–liquid equilibrium occurs in leaching, crystallization, and adsorption. In leaching it is common to assume that all solute is dissolved in the solvent and that the remaining solid in the underflow is accompanied by a known fraction of liquid. Crystallization calculations are best made with a phase-equilibrium diagram. For crystallization of salts from an aqueous solution, formation of hydrates must be considered. Adsorption can be represented algebraically or graphically by adsorption isotherms.
8. Solubility of gases that are only sparingly soluble in a liquid are well represented by a Henry's law constant that depends on temperature.
9. Solid vapor pressure can determine equilibrium sublimation and desublimation conditions for gas–solid systems. Adsorption isotherms and y – x diagrams are useful in adsorption-equilibrium calculations for gas mixtures in the presence of solid adsorbent.
10. Calculations of multiphase equilibrium are best made by process simulators. However, manual procedures are available for vapor–liquid–solid systems when no component is found in all phases, and to vapor–liquid–liquid systems when only one component distributes in all phases.

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