

# Chapter 2

## Equilibria, Bubble Points, Dewpoints, Flash Calculations, and Activity Coefficients

### 2.1 Vapour Pressure Calculations

The basis for all phase equilibrium calculations are the vapour pressures of the components. The vapour pressure is derived using the Antoine Equation and Antoine Constants  $A$ ,  $B$ , and  $C$ .

$$\text{Antoine Equation : } \lg p_0 = \frac{A - B}{C + t(^{\circ}\text{C})}$$

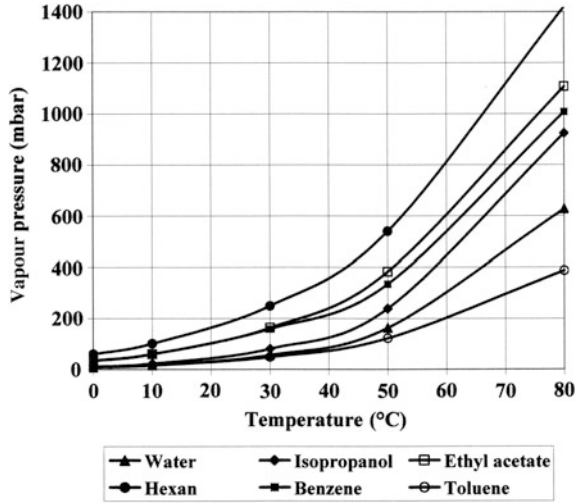
**Example 1.1:** Calculation of the vapour pressures of benzene and toluene (Fig. 2.1).

	Benzene	Toluene
	$A = 7.00481$	$A = 7.07581$
	$B = 1196.76$	$B = 1342.31$
	$C = 219.161$	$C = 219.187$
Temperature	Benzene vapour pressure	Toluene vapour pressure
50 °C	$p_{0B} = 362 \text{ mbar}$	$p_{0T} = 123 \text{ mbar}$
98 °C	$p_{0B} = 1704 \text{ mbar}$	$p_{0T} = 698 \text{ mbar}$
103 °C	$p_{0B} = 1950 \text{ mbar}$	$p_{0T} = 812 \text{ mbar}$

### 2.2 Phase Equilibrium of Ideal Binary Mixtures

The equilibrium between the liquid and the vapour phase is calculated according to the laws of Dalton and Raoult.

**Fig. 2.1** Vapour pressure of different components as a function of temperature



**Dalton:**

$$p_1 = y_1 * P_{\text{tot}} \quad P_{\text{tot}} = p_1 + p_2 + p_3 + \dots p_i$$

**Raoult** (Fig. 2.2):

$$p_1 = x_1 * p_{01} \quad p_2 = x_2 * p_{02}$$

$$P_{\text{tot}} = x_1 * p_{01} + x_2 * p_{02} + x_3 * p_{03} + \dots x_i * p_{0i}$$

**Equilibrium equation:**  $y_i * P_{\text{tot}} = p_i = x_i * p_{0i}$

$$y_i = \frac{x_i * p_{0i}}{P_{\text{tot}}} = \frac{p_i}{P_{\text{tot}}}$$

$y_i$  = concentration of the component  $i$  in the vapour phase (mole fraction)

$x_i$  = concentration of the component  $i$  in the liquid phase (mole fraction)

$P_{\text{tot}}$  = total pressure (mbar)

$p_{0i}$  = vapour pressure of the component  $i$  (mbar)

$p_i$  = partial pressure of the component  $i$  (mbar)

**Example 2.2.1:** Calculation of the partial pressures and the vapour compositions for an ideal binary mixture.

$$x_1 = 0.6 \quad p_{01} = 800 \text{ mbar}$$

$$x_2 = 0.4 \quad p_{02} = 1300 \text{ mbar}$$

Calculation of the partial pressures according to Raoult:

$$\begin{aligned} p_1 &= x_1 * p_{01} = 0.6 * 800 = 480 \text{ mbar} \\ p_2 &= x_2 * p_{02} = 0.4 * 1300 = 520 \text{ mbar} \\ P_{\text{tot}} &= 1000 \text{ mbar} \end{aligned}$$

Calculation of the vapour concentration according to Dalton:

$$\begin{aligned} y_1 &= \frac{p_1}{P_{\text{tot}}} = \frac{480}{1000} = 0.48 \text{ molfr.} = 48 \text{ mol\%} \\ y_2 &= \frac{p_2}{P_{\text{tot}}} = \frac{520}{1000} = 0.52 \text{ molfr.} = 52 \text{ mol\%} \end{aligned}$$

In order to simplify the calculation of phase equilibria a separation factor  $\alpha$  is introduced, often also called the relative volatility  $\alpha$ , defined as the ratio of the vapour pressures of the two components, or the ratio of the equilibrium constants,  $K$ , of the components of the ideal mixture.

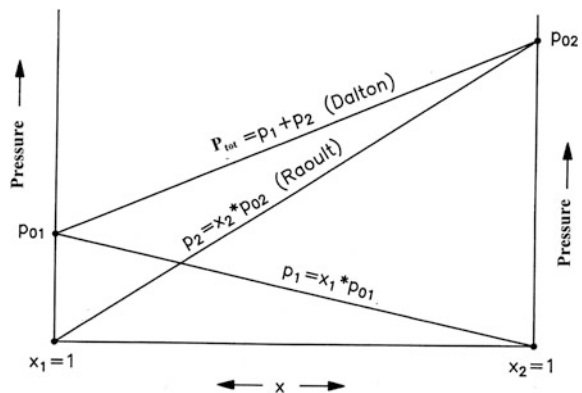
$$\alpha_{1/2} = \frac{P_{01}}{P_{02}} = \frac{K_1}{K_2}$$

Calculation with the relative volatility  $\alpha$  assumes that both vapour pressure curves are fairly parallel in the logarithmic representation (see Fig. 2.3).

In Fig. 2.4 it can be seen that the relative volatility becomes smaller with rising temperatures. The separation becomes more difficult with increasing temperatures.

Due to the fact that the relative volatility in the rectification section, and in the stripping section, is different, a geometrical average is formed from the separation factor  $\alpha_V$  in the rectification section and the separation factor  $\alpha_A$  in the stripping section.

**Fig. 2.2** Graphical representation of the laws of Dalton and Raoult for an ideal mixture



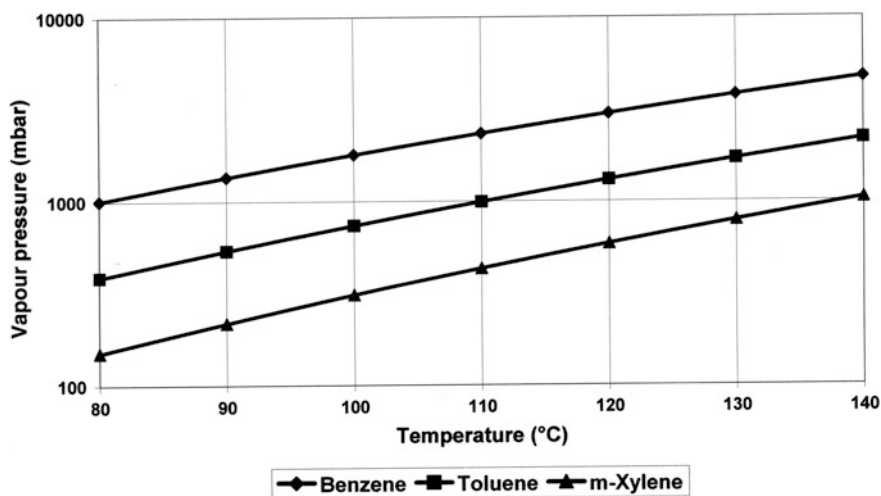


Fig. 2.3 Vapour pressure curves of benzene, toluene, and xylene

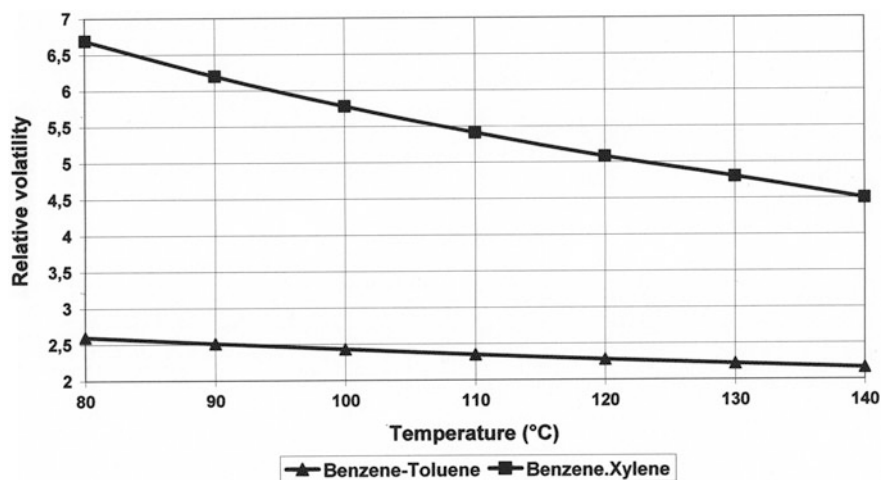


Fig. 2.4 Relative volatilities for the separation of benzene/toluene and benzene/xylene as a function of temperature

$$\alpha_{av} = \sqrt{\alpha_V * \alpha_A}$$

Using the relative volatility  $\alpha$  one gets a very simple equation for the calculation of the phase equilibrium between the composition in the vapour and the composition in the liquid.

$$y = \frac{\alpha * x}{1 + (\alpha - 1) * x} \quad (\text{molfraction}) \qquad x = \frac{y}{\alpha - (\alpha - 1) * y} \quad (\text{molfraction})$$

**Example 2.2.2:** Calculation of the vapour composition  $y_1$  for a liquid composition of  $x_1 = 0.2$ .  $p_{01} = 400$  mbar  $p_{02} = 200$  mbar  $x_1 = 0.2$   $x_2 = 0.8$

$$\alpha = \frac{400}{200} = 2$$

$$y_1 = \frac{\alpha * x_1}{1 + (\alpha - 1) * x_1} = \frac{2 * 0.2}{1 + (2 - 1) * 0.2} = 0.33 \text{ molfr.}$$

$$P_{\text{tot}} = x_1 * p_{01} + x_2 * p_{02} = 0.2 * 400 + 0.8 * 200 = 240 \text{ mbar}$$

$$y_1 = \frac{x_1 * p_{01}}{P_{\text{tot}}} = \frac{0.2 * 400}{240} = 0.33 \text{ molfr.}$$

**Cross-check calculation for  $x$ :**

$$x_1 = \frac{y_1}{\alpha - (\alpha - 1) * y_1} = \frac{0.33}{2 - (2 - 1) * 0.33} = 0.2 \text{ molfr.}$$

$$x_1 = \frac{y_1 * P_{\text{tot}}}{p_{01}} = \frac{0.33 * 240}{400} = 0.2 \text{ molfr.}$$

In American literature the equilibrium constant  $K$ , which is defined as the ratio of the compositions in vapour and liquid, is often used instead of the relative volatility  $\alpha$ .

$$K = \frac{y_i}{x_i} = \frac{p_{0i}}{P_{\text{ges}}}$$

$$y_1 = K_1 * x_1 = K_1 * \frac{1 - K_2}{K_1 - K_2}$$

$$x_1 = \frac{y_1}{K_1} = \frac{1 - K_2}{K_1 - K_2}$$

**Example 2.2.3: Equilibrium calculation with the equilibrium constant  $K$ .**

$$x_1 = 0.6 \quad p_{01} = 800 \text{ mbar} \quad p_1 = 0.6 * 800 = 480 \text{ mbar}$$

$$x_2 = 0.4 \quad p_{02} = 1300 \text{ mbar} \quad p_2 = 0.4 * 1300 = 520 \text{ mbar} \quad P_{\text{tot}} = 1000 \text{ mbar}$$

**Calculation of the equilibrium factor  $K$ :**

$$K_1 = \frac{y_1}{x_1} = \frac{p_{01}}{P_{\text{tot}}} = \frac{800}{1000} = 0.8$$

$$K_2 = \frac{y_2}{x_2} = \frac{p_{02}}{P_{\text{tot}}} = \frac{1300}{1000} = 1.3$$

**Calculation of the vapour composition  $y$ :**

$$y_1 = K_1 * x_1 = 0.8 * 0.6 = 0.48 \text{ molfr.}$$

$$y_1 = K_1 * \frac{1 - K_2}{K_1 - K_2} = 0.8 * \frac{1 - 1.3}{0.8 - 1.3} = 0.48 \text{ molfr.}$$

**Cross-check calculation of  $x_1$ :**

$$x_1 = \frac{y_1}{K_1} = \frac{0.48}{0.8} = 0.6 \text{ molfr.}$$

$$x_1 = \frac{1 - K_2}{K_1 - K_2} = \frac{1 - 1.3}{0.8 - 1.3} = 0.6 \text{ molfr.}$$

## 2.3 Bubble Point Calculation

The bubble point of a mixture is defined as follows:

$$\sum y_i = \sum K_i * x_i = 1$$

The bubble pressure  $P_{\text{boil}}$  can be calculated directly.

$$P_{\text{boil}} = x_1 * p_{01} + x_2 * p_{02}$$

A simple method for calculating the bubble temperature of a mixture is the calculation of the bubble pressure from the sum of the partial pressures.

At the bubble temperature the bubble point pressure must be equal to the system pressure  $P_{\text{tot}}$ . The following example shows the procedure.

### **Example 3.1: Iterative bubble point calculation for a benzene-toluene mixture**

30 mol% benzene in the liquid phase ( $x = 0.3$ )

70 mol% toluene in the liquid phase ( $x = 0.7$ )

$P_{\text{tot}} = 1000 \text{ mbar}$   $p_{0B}$  = vapor pressure of benzene

$p_{0T}$  = vapor pressure of toluene

First choice :  $t = 95^\circ\text{C}$        $p_{0B} = 1573 \text{ mbar}$        $p_{0T} = 634.4 \text{ mbar}$

$P_{\text{boil}} = 0.3 * 1573 + 0.7 * 634.4 = 916 \text{ mbar}$        $P_{\text{boil}}$  is too low!

Second choice :  $t = 100^\circ\text{C}$        $p_{0B} = 1807 \text{ mbar}$        $p_{0T} = 740 \text{ mbar}$

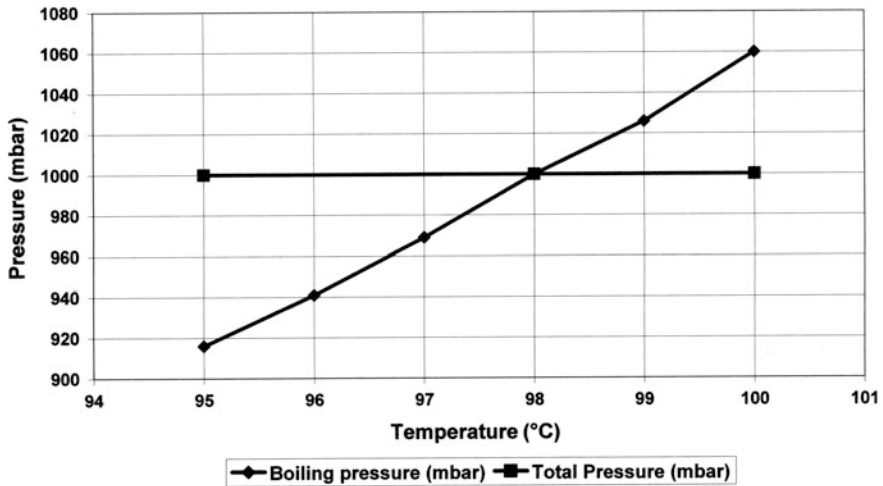


Fig. 2.5 Bubble point determination by graphical interpolation

$$P_{\text{boil}} = 0.3 * 1807 + 0.7 * 740 = 1060 \text{ mbar}$$

$P_{\text{boil}}$  is too high!

Third choice :  $t = 98^\circ\text{C}$        $p_{0\text{B}} = 1710 \text{ mbar}$

$p_{0\text{T}} = 696 \text{ mbar}$

$$P_{\text{boil}} = 0.3 * 1710 + 0.7 * 696 = 1000 \text{ mbar}$$

$P_{\text{boil}} = 1000 \text{ mbar} = \text{correct!}$

Figure 2.5 shows how the bubble point determination can be simplified by graphical interpolation. The sum of the two partial pressures must be equal to the system pressure.

#### Cross-check calculation of the bubble point at 98 °C:

Vapour pressure of benzene  $p_{0\text{B}} = 1710 \text{ mbar}$

Vapour pressure of toluene  $p_{0\text{T}} = 696 \text{ mbar}$

$$K_1 = \frac{p_{0\text{B}}}{P_{\text{tot}}} = \frac{1710}{1000} = 1.71$$

$$K_2 = \frac{p_{0\text{T}}}{P_{\text{tot}}} = \frac{696}{1000} = 0.696$$

$$\sum K_i = K_1 * x_1 + K_2 * x_2 = 1.71 * 0.3 + 0.696 * 0.7 = 1$$

The bubble point specification is therefore fulfilled.

## 2.4 Dew Point Calculation

The dew point of a mixture is defined as follows:

$$\sum x_i = \sum y_i/K_i = 1$$

The dew point pressure  $P_{\text{dew}}$  can be calculated directly.

$$\frac{1}{P_{\text{dew}}} = \frac{y_1}{p_{01}} + \frac{y_2}{p_{02}} \quad P_{\text{dew}} = \left[ \sum \frac{y_i}{p_{0i}} \right]^{-1}$$

The dew point temperature for a specific pressure is calculated iteratively until the sum of the quotients  $y_i/p_{0i}$  is equal to the reciprocal value of the system pressure  $P_{\text{tot}}$ . The following example shows the procedure.

**Example 2.4.1: Iterative dew point calculation for a benzene-toluene mixture.**

30 mol% benzene in the vapour phase ( $y = 0.3$ )

70 mol% toluene in the vapour phase ( $y = 0.7$ )

$P_{\text{tot}} = 1000 \text{ mbar}$

First choice :  $t = 100^\circ\text{C}$        $p_{0\text{B}} = 1807 \text{ mbar}$        $p_{0\text{T}} = 740 \text{ mbar}$

$$\frac{1}{P_{\text{dew}}} = \frac{y_1}{p_{01}} + \frac{y_2}{p_{02}} = \frac{0.3}{1807} + \frac{0.7}{740} = 0.0011 \quad P_{\text{dew}} = 899 \text{ mbar is too low!}$$

Second choice :  $t = 104^\circ\text{C}$        $p_{0\text{B}} = 2013 \text{ mbar}$        $p_{0\text{T}} = 834.4 \text{ mbar}$

$$\frac{1}{P_{\text{dew}}} = \frac{y_1}{p_{01}} + \frac{y_2}{p_{02}} = \frac{0.3}{2013} + \frac{0.7}{834.4} = 0.00099 \quad P_{\text{dew}} = 1012 \text{ mbar is too high!}$$

Third choice :  $t = 103.8^\circ\text{C}$        $p_{0\text{T}} = 2002 \text{ mbar}$        $p_{0\text{T}} = 829 \text{ mbar}$

$$\frac{1}{P_{\text{dew}}} = \frac{y_1}{p_{01}} + \frac{y_2}{p_{02}} = \frac{0.3}{2002} + \frac{0.7}{829} = 0.001 \quad P_{\text{ges}} = 1000 \text{ mbar is correct!}$$

**Cross-check calculation for the dew point at  $103.8^\circ\text{C}$ :**

$$K_1 = \frac{2002}{1006} = 1.99 \quad K_2 = \frac{829}{1006} = 0.824$$

$$\sum \frac{y_i}{K_i} = \frac{0.3}{1.99} + \frac{0.7}{0.824} = 1$$

The condition for the dew point is fulfilled.

Figure 2.6 shows how the dew point can be determined by graphical interpolation.



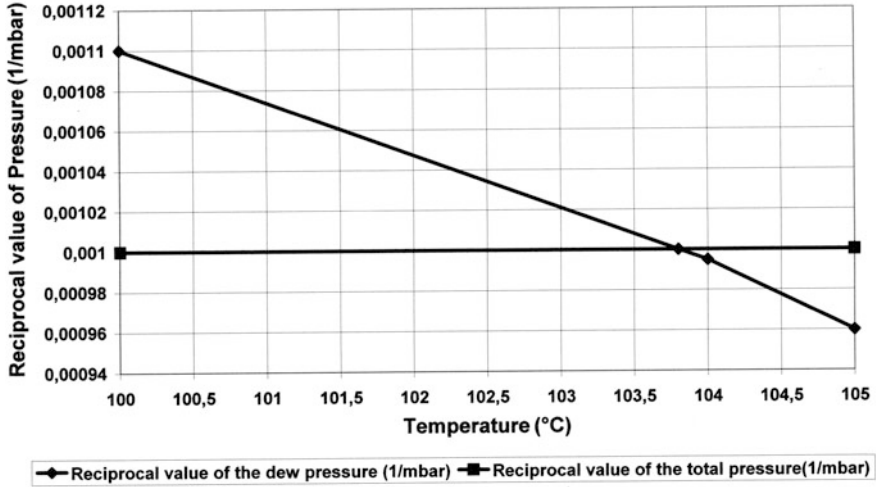


Fig. 2.6 Dew point determination by graphical interpolation

## 2.5 Dew Point Calculation of Vapour Containing Inert Gases

The dew point of a vapour mixture containing inert gas is reached if the sum of the partial pressures of the vapours ( $\sum y_i * P_{ges}$ ) reaches the vapour pressure of the liquid phase by cooling.

$$\sum y_i * P_D = \sum z_i * P_{tot} = \sum x_i * p_{0i}$$

$$P_D = P_{tot} - P_{IN}$$

$P_D$  = sum of the vapours partial pressures (mbar)

$P_{IN}$  = inert gas partial pressure (mbar)

$P_{tot}$  = total pressure in the system with inert gas (mbar)

$y_i$  = vapour composition based on the vapour partial pressure  $P_D$

$z_i$  = vapour composition based on the total pressure  $P_{tot}$  with inert gas

**Calculation of the dew point pressure without inert gas:**

$$P_{dew} = \left( \sum \frac{y_i}{P_{0i}} \right)^{-1} \quad \sum \frac{y_i}{K_i} = 1 \quad K_i = \frac{P_{0i}}{P_D}$$

**Calculation of the dew point pressure with inert gas:**

$$P_{\text{dew}} = \left( \sum \frac{z_i}{P_{0i}} \right)^{-1} \quad \sum \frac{z_i}{K_i} = 1 \quad K_i = \frac{P_{0i}}{P_{\text{tot}}}$$

**Example 2.5.1: Dew point pressure calculation without inert gas.**

$$y_1 = 0.413 \quad P_{01} = 3009.3 \text{ mbar at } 102^\circ \text{C}$$

$$y_2 = 0.587 \quad P_{02} = 830.8 \text{ mbar}$$

$$P_{\text{dew}} = \left[ \sum \frac{y_i}{P_{0i}} \right]^{-1} = \left[ \frac{0.413}{3009.3} + \frac{0.587}{830.8} \right]^{-1} = 1185 \text{ mbar}$$

$$K_1 = \frac{3009.3}{1185} = 2.54 \quad K_2 = \frac{830.8}{1185} = 0.7$$

$$\sum x_i = \frac{0.413}{2.54} + \frac{0.587}{0.7} = 1$$

**Example 2.5.2: Dew point pressure calculation with inert gas.**

40 Vol% vapour + 60 Vol% inert gas

$$y_1 = 0.413 \text{ molfr.} \quad P_{01} = 3009.3 \text{ mbar at } 102^\circ \text{C}$$

$$y_2 = 0.587 \text{ molfr.} \quad P_{02} = 830.8 \text{ mbar}$$

$$z_1 = 0.4 * y_1 = 0.4 * 0.413 = 0.165 \text{ molfr.}$$

$$z_2 = 0.4 * y_2 = 0.4 * 0.587 = 0.235 \text{ molfr.}$$

$$\text{Vapour fraction : } \sum z_1 + z_2 = 0.4$$

$$\text{Inert gas fraction : } z_{\text{IN}} = 0.6$$

$$P_{\text{dew}} = \left[ \sum \frac{z_i}{P_{0i}} \right]^{-1} = \left[ \frac{0.165}{3009.3} + \frac{0.235}{830.8} \right]^{-1} = 2961.3 \text{ mbar}$$

$$K_1 = \frac{3009.3}{2961.3} = 1.016 \quad K_2 = \frac{830.8}{2961.3} = 0.28$$

$$\sum x_i = \frac{0.165}{1.016} + \frac{0.235}{0.28} = 1$$

With inert gas the dew point pressure is much higher and the dew point temperature lies lower than it would without inert gas. In addition, with inert gas in the vapour a much deeper cooling must take place in order to condense the vapour.

## 2.6 Dew and Bubble Point Lines of Ideal Binary Mixtures

The bubble point of a liquid mixture is defined such that the sum of the partial pressures of the mixture reaches the system pressure with the first droplet being evaporated. Due to the preferred evaporation of light-boiling components, high-boiling components increase in concentration and the bubble point rises. The curve of the boiling temperature as a function of the composition of the light-boiling components in the mixture is known as the boiling line.

**Equation for the boiling point line:**

$$x_1 = f(t) = \frac{P_{\text{tot}} - p_{02}}{p_{01} - p_{02}} \quad (\text{molfraction light boilers in the liquid})$$

The boiling point temperature increases with decreasing composition of light-boiling components.

The dew point of a vapour mixture is the temperature at which the first droplet is condensed. Due to the preferred condensing of high-boiling components the vapour mixture is enriched with light-boiling components and the dew point temperature drops.

The representation of the dew point temperature as function of the vapour composition is referred to as the dew point line.

**Equation for the dew point line:**

$$y_1 = f(t) = \frac{p_{01}}{P_{\text{tot}}} * \frac{P_{\text{tot}} - p_{02}}{p_{01} - p_{02}} \quad (\text{molfraction light boilers in the vapor})$$

A diagram with bubble and dew point lines is called a phase diagram or temperature–composition diagram.

**Example 2.6.1: Construction of the temperature–composition diagram for benzene [1]–toluene [2] at 1013 mbar**

**Procedure:**

1. Calculation of the two boiling points with the Antoine Equation.  
The **two boiling points are the end points** in the temperature–composition diagram.  
Bubble point of benzene: 80.1 °C  
Bubble point of toluene: 110.6 °C
2. Calculation of vapour pressures at different temperatures with the Antoine equation.
3. Determination of the liquid composition  $x$  and the vapour composition  $y$  at the different temperatures using the equations for the bubble and dew point lines.

Calculation results:

Temperature (°C)	$p_{01}$ (mbar)	$p_{02}$ (mbar)	$x_1$ (molfr.)	$y_1$ (molfr.)
80.1	1013	390	1.000	1.000
83	1107	430	0.861	0.941
86	1211	476	0.731	0.874
89	1322	525	0.612	0.799
92	1442	578	0.504	0.717
95	1569	636	0.404	0.626
98	1705	698	0.313	0.527
101	1850	765	0.229	0.418
104	2004	836	0.151	0.300
107	2168	913	0.080	0.170
110.6	2378	1013	0.0	0.0

**Bubble point line** :  $x_1 = f(\text{temperature})$       **Dew point line** :  $y_1 = f(\text{temperature})$

$p_{01}$  = vapour pressure of benzene    $p_{02}$  = vapour pressure of toluene  
 $x_1$  = liquid composition of the lighter boiling component of benzene (molfraction)  
 $y_1$  = vapour composition of the lighter boiling component benzene (molfraction)

Figure 2.7 depicts the temperature–composition diagram of the benzene–toluene mixture.

The dew point of a vapour mixture with 30 mol% benzene and 70 mol% toluene lies at 104 °C. The bubble point of the mixture lies at 98 °C. The first liquid droplet

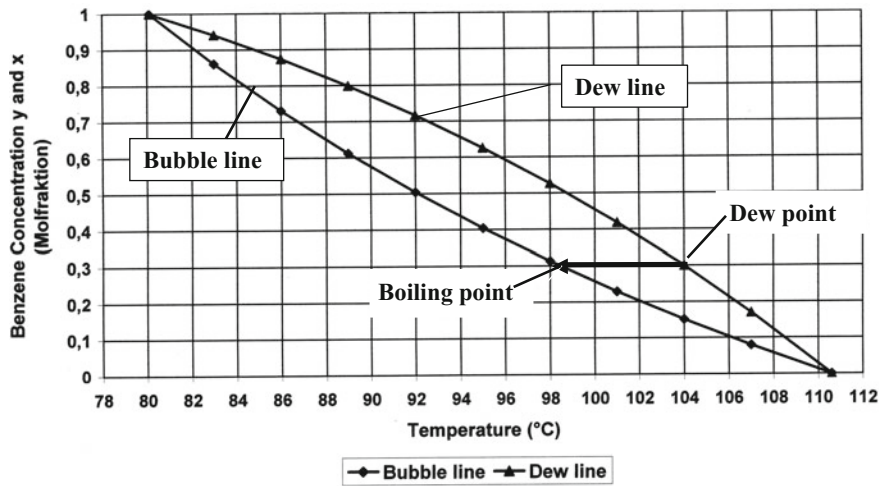


Fig. 2.7 Temperature–composition diagram for the benzene–toluene mixture

condenses at a 104 °C dew point. At the bubble point of 98 °C the total mixture is liquid. In order to condense the total mixture the mixture has to be cooled down from 104 to 98 °C. When evaporating, the mixture must on the contrary be heated from the bubble point to the dew point.

## 2.7 The Bubble Point and Dew Point of Immiscible Mixtures

One example of common mixtures of this type is the mixture of hydrocarbons and water. In an immiscible mixture both liquid phases exert temperature dependent vapour pressures.

### Bubble point:

The bubble point pressure  $P_{\text{boil}}$  results from the sum of the hydrocarbon vapour pressures  $P_{\text{org}}$  and the water vapour pressures  $P_{\text{W}}$ .

$$P_{\text{boil}} = P_{\text{org}} + P_{\text{W}}$$

This equation is the foundation for steam stripping.

By introducing water or steam the bubble point of hydrocarbons is reduced.

### Example 2.7.1: Bubble point of a toluene–water mixture at 1010 mbar.

Temperature: 84 °C.

Toluene vapour pressure at 84 °C = 444 mbar.

Water vapour pressure at 84 °C = 566 mbar.

$$P_{\text{boil}} = 444 + 566 = 1010 \text{ mbar.}$$

### The bubble point for the toluene–water mixture is 84 °C at 1010 mbar.

### Dew point:

In the dew point calculation the composition of the vapour is used as opposed to the bubble point calculation. The dew point is defined as the point at which the partial pressure equals the vapour pressure of the respective component. In a vapour mixture the component that first condenses out is the component whose partial pressure reaches the vapour pressure of the component. The higher the vapour composition the higher the partial pressure and the earlier condensing out of the component occurs.

$$P_{\text{org}} = y_{\text{org}} * P_{\text{tot}} \quad P_{\text{W}} = y_{\text{W}} * P_{\text{tot}}$$

The dew point is reached when the vapour pressure of the component falls below the partial pressure of the component.

- $P_{0\text{org}} < P_{\text{org}}$  The vapour pressure of the organic component is lower than the partial pressure, leading to the dew point of the organic component.
- $P_{0\text{W}} < P_{\text{W}}$  The vapour pressure of water is lower than the partial pressure, leading to the dew point of water.

**Example 2.7.2: Determination of the dew point of a toluene–water mixture.**

**(a) Water condenses first:**

Water vapour composition in the vapour  $y_{\text{W}} = 0.63$ ;  $P_{\text{tot}} = 1$  bar.

Water vapour partial pressure  $P_{\text{W}} = 0.63 * 1000 = 630$  mbar.

Water has a vapour pressure of  $P_{0\text{W}} = 630$  mbar at  $87.2$  °C.

The dew point is  $87.2$  °C.

Water condenses first.

**(b) Toluene condenses first:**

Toluene composition in the vapour  $y_{\text{org}} = 0.578$ ;  $P_{\text{tot}} = 1$  bar.

Toluene partial pressure  $P_{\text{org}} = 0.578 * 1000 = 578$  mbar.

Toluene has a vapour pressure of  $P_{0\text{org}} = 578$  mbar at  $92$  °C.

The dew point is  $92$  °C.

Toluene condenses first.

## 2.8 Flash Calculations for Ideal Binary Mixtures [1]

At the bubble point the total mixture is liquid.

At the dew point the total mixture is vapour.

The vapour and liquid rates change between bubble point and dew point.

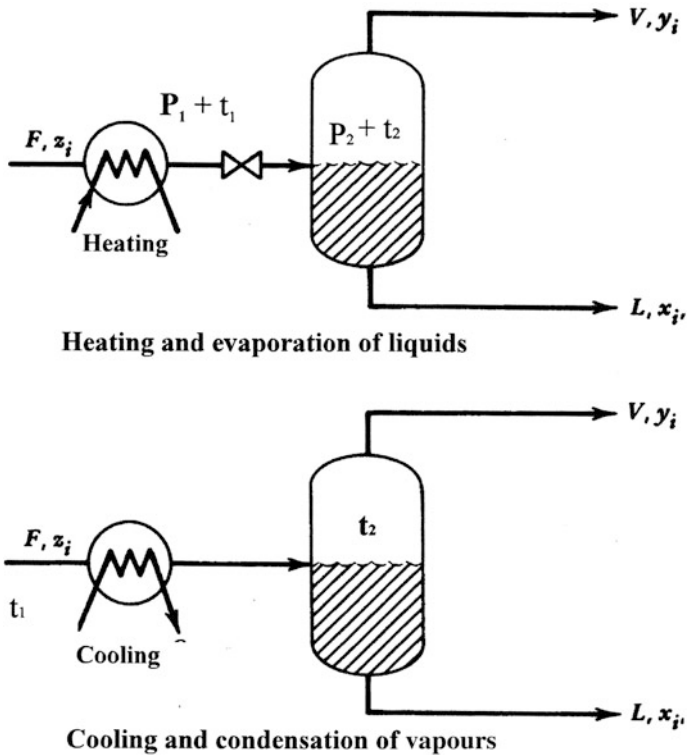
When heated to  $t_1$  and vaporized at pressure  $P_2$  a part of the liquid will be vaporized (Fig. 2.8).

When cooling the vapour mixture to the temperature  $t_2$  a part of the vapour condenses (Fig. 2.8).

Using the flash calculation the vapour composition of the mixture at temperatures between bubble point and dew point is calculated. The compositions in the vapour and liquid phase when cooling or heating are also determined with the equilibrium factors.

### How much of the mixture is vapour at temperatures between bubble point and dew point?

The calculation of the vapour fraction  $V$  of the feed  $F$  is accomplished with the use of the equilibrium constants  $K_1$  and  $K_2$  for the vapour composition of the light-boiling component  $z_1$  as follows:



**Fig. 2.8** Flash separation after heating liquid mixtures or cooling vapour mixtures

$$\frac{V}{F} = \frac{z_1 * \frac{K_1 - K_2}{1 - K_2} - 1}{K_1 - 1}$$

**What is the composition of the liquid and vapour fractions of the mixture?**

$$x_1 = \frac{1 - K_2}{K_1 - K_2}$$

$$y_1 = K_1 * x_1$$

$V$  = vapour rate (kmol/h).

$F$  = feed rate (kmol/h).

$K_1$  = equilibrium constant of the lighter component 1.

$K_2$  = equilibrium constant of the heavier component 2.

$z_1$  = composition of the lighter component 1 in the feed (molfraction).

$x_1$  = composition of the lighter component in the liquid phase (molfraction).

$y_1$  = composition of the lighter component in the vapour (molfraction).

**Example 2.8.1: Flash calculations for a benzene–toluene mixture with  $z_1 = 0.3 = 30 \text{ mol\%}$  benzene in the vapour.**

At the bubble point (98 °C) all is liquid.

At the dew point (104 °C) all is vapor.

Feed composition: 30 mol% benzene ( $z = 0.3 \text{ molfr.}$ ).

**The vapour fraction at 100 °C has to be calculated:**

$$t = 100 \text{ °C.}$$

$$P_{\text{tot}} = 1000 \text{ mbar.}$$

$$\text{Vapour pressure of benzene } p_{0B} = 1807 \text{ mbar.}$$

$$\text{Vapour pressure of toluene } p_{0T} = 740 \text{ mbar.}$$

$$P_{\text{tot}} = 1000 \text{ m.}$$

$$\text{Benzene } K_1 = \frac{p_{0B}}{P_{\text{tot}}} = \frac{1807}{1000} = 1.807$$

$$\text{Toluene } K_2 = \frac{p_{0T}}{P_{\text{tot}}} = \frac{740}{1000} = 0.74$$

$$\frac{V}{F} = \frac{0.3 * \frac{1.807-0.74}{1-0.74} - 1}{1.807 - 1} = 0.2864$$

Therefore, 28.64 mol% from the feed is vapour at 100 °C!

**Calculation of the compositions in liquid and vapour at  $t = 100 \text{ °C}$ :**

$$x_1 = \frac{1 - 0.74}{1.807 - 0.74} = 0.2437$$

→ 24.37 mol% benzene in the liquid.

$$y_1 = 1.807 * 0.2437 = 0.44$$

→ 44 mol% benzene in the vapour phase.

For the design of condensers and reboilers for mixtures the condensation curve or the flash curve is required.

In these curves the vapour fraction  $V/F$  of the mixture based on the feed rate  $F$  is plotted over the temperature of the mixture.

**Example 2.8.2: Calculation of the condensation curve for the mixture benzene–o–xylene.**

Inlet composition:  $z = 0.576 = 57.6 \text{ mol\%}$  benzene with vapour mixture.

$T \text{ (°C)}$	$K_1$	$K_2$	$V/F$	$x_1$	$y_1$
96	1.57	0.22	0	0.576	0.906
98.9	1.74	0.25	0.2	0.502	0.874
104	2	0.3	0.4	0.41	0.82
110.2	2.34	0.37	0.6	0.318	0.748
116.2	2.72	0.448	0.8	0.242	0.66
121	3.07	0.52	1	0.188	0.576



**Calculation at  $T = 96^\circ\text{C}$ :**

$$\frac{V}{F} = \frac{z_1 * \frac{K_1 - K_2}{1 - K_2} - 1}{K_1 - 1} = \frac{0.576 * \frac{1.57 - 0.22}{1 - 0.22} - 1}{1.57 - 1} = 0$$

$$x_1 = \frac{1 - K_2}{K_1 - K_2} = \frac{1 - 0.22}{1.57 - 0.22} = 0.576 \quad y_1 = K_1 * x_1 = 1.57 * 0.576 = 0.906$$

**Calculation at  $T = 98.9^\circ\text{C}$ :**

$$\frac{V}{F} = \frac{0.576 * \frac{1.74 - 0.25}{1 - 0.25} - 1}{1.74 - 1} = 0.2$$

$$x_1 = \frac{1 - 0.25}{1.74 - 0.25} = 0.502 \quad y_1 = 1.74 * 0.502 = 0.874$$

**Calculation at  $T = 116.2^\circ\text{C}$ :**

$$\frac{V}{F} = \frac{0.576 * \frac{2.72 - 0.448}{1 - 0.448} - 1}{2.72 - 1} = 0.8$$

$$x_1 = \frac{1 - 0.448}{2.72 - 0.448} = 0.242 \quad y_1 = 2.72 * 0.242 = 0.66$$

**Calculation at  $T = 121^\circ\text{C}$ :**

$$\frac{V}{F} = \frac{0.576 * \frac{3.07 - 0.52}{1 - 0.52} - 1}{3.07 - 1} = 1$$

$$x_1 = \frac{1 - 0.52}{3.07 - 0.52} = 0.188 \quad y_1 = 3.07 * 0.188 = 0.576$$

The condensation curve for the benzene–o-xylene mixture is depicted in Fig. 2.9. The molar vapour fraction  $V/F$  drops from  $V/F = 1$  at dew point at  $121^\circ\text{C}$  to  $V/F = 0$  at bubble point  $96^\circ\text{C}$ . The concentration of the light components of benzene in the vapour and liquid phase against temperature are plotted in Fig. 2.10.

The required heat loads for the condensation of the benzene–o-xylene mixture result from the enthalpies for the cooling of the vapour mixture along with the condensing and the cooling of the condensate. Figure 2.11 gives the calculated heat loads for condensing a mixture of 1000 kg/h benzene and 1000 kg/h o-xylene as function of temperature. In condensing and cooling from the dew point ( $121^\circ\text{C}$ ) to the bubble point ( $96^\circ\text{C}$ ) of the mixture the required heat load increases from 0 to 230 kW.

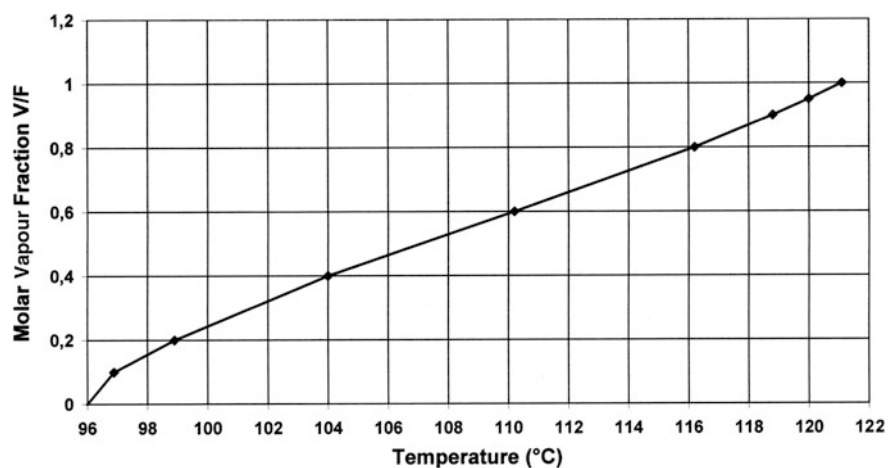


Fig. 2.9 Condensation curve for the benzene-o-xylene mixture given in Example 2.8.2

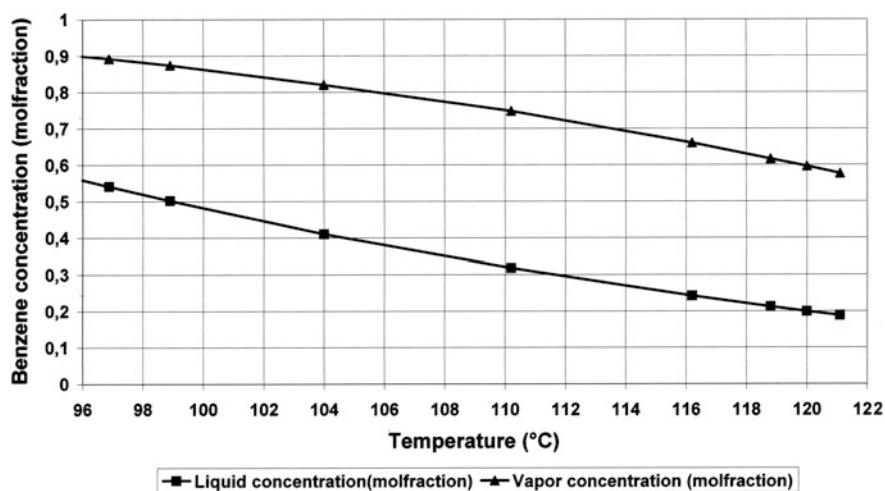
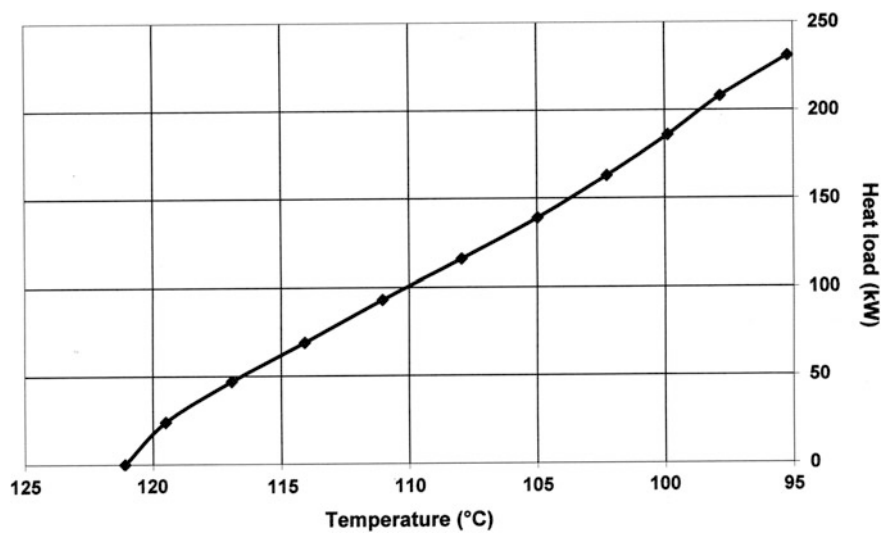


Fig. 2.10 Benzene compositions in the vapour and liquid phase as function of temperature



**Fig. 2.11** Heat load *curve* for the condensation of 2 tonnes/h of the benzene–o–xylene mixture as a function of temperature

**Example 2.8.3: Flash calculations for a mixture of 30 mol% butane and 70 mol% pentane.**

Pressure (bar)	Boiling point temperature (°C)	Dew point temperature (°C)
	$x_{\text{But}} = 0.3$ $x_{\text{Pen}} = 0.7$	$y_{\text{But}} = 0.3$ $y_{\text{Pen}} = 0.7$
1	19.5	28.9
2	41	50
3	55.3	64
4	66.3	74.7

**Flash calculation at 4 bar:**

Temperature (°C)	Molar ratio $V/F$
66	0.0
67	0.061
68	0.149
69	0.242
70	0.341
71	0.448
72	0.567
73	0.703
74	0.861
75	1.0

$V$  = vapour rate (kmol/h);  $F$  = feed rate (kmol/h)

Figure 2.12 depicts the bubble points and dew points of the mixture as a function of pressure.

The flash curve of the mixture of 30 mol% butane and 70 mol% pentane at a pressure of 4 bar is shown in Fig. 2.13.

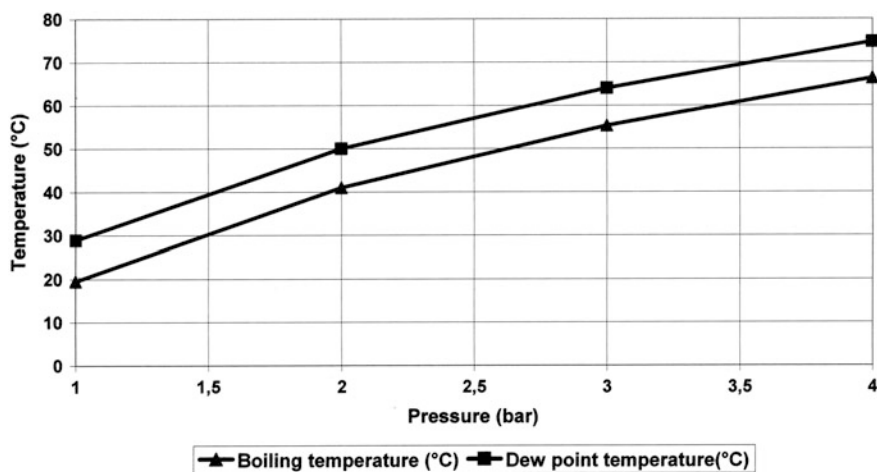


Fig. 2.12 Bubble points and dew points of the butane–pentane mixture as function of pressure

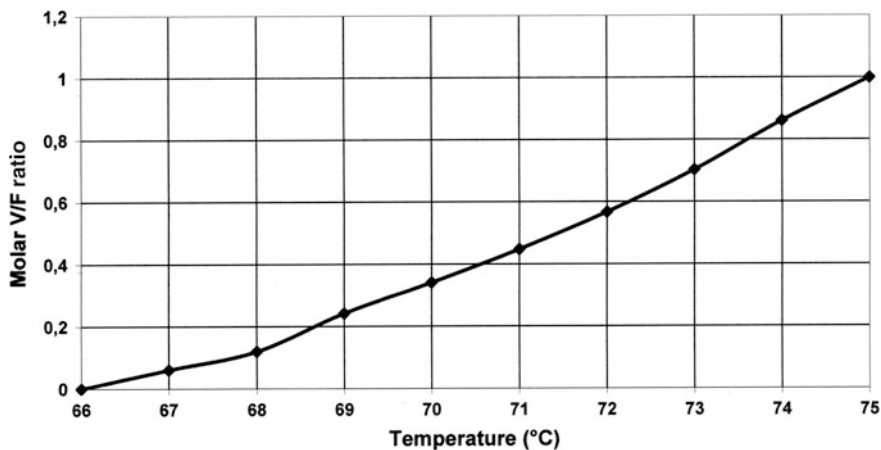


Fig. 2.13 Flash curve for the V/F ratio of the butane–pentane mixture at 4 bar as a function of temperature

## 2.9 Calculation of the Equilibrium and the Bubble and Dew Point Temperatures of Ideal Multi-component Mixtures

In principle the same laws and equations hold as in the calculations for binary component mixtures.

$$P_{\text{tot}} = x_1 * p_{01} + x_2 * p_{02} + x_3 * p_{03} + x_i * p_{0i}$$

$$y_i = K_i * x_i = x_i * \frac{p_{0i}}{P_{\text{tot}}} \quad x_i = y_i * \frac{P_{\text{tot}}}{p_{0i}} = \frac{y_i}{K_i}$$

With the relative volatility  $\alpha$  based on the vapour pressure  $p_{0h}$  of the heaviest component

$$\alpha_1 = \frac{p_{01}}{p_{0h}} \quad \alpha_2 = \frac{p_{02}}{p_{0h}} \quad \alpha_3 = \frac{p_{03}}{p_{0h}}$$

$$y_1 = \frac{\alpha_1 * x_1}{\sum (\alpha_i * x_i)} = \frac{\alpha * x}{\sum \alpha_i * x_i}$$

$$x_1 = \frac{y_1 / \alpha_1}{\sum (y_i / \alpha_i)} = \frac{y / \alpha}{\sum y_i / \alpha_i}$$

**Example 2.9.1: Calculation of the vapour phase composition for a benzene–toluene–xylene mixture.**

Benzene : 30 mol%     $x_1 = 0.3$      $p_{01} = 1795$  mbar at 100 °C  
 Toluene : 60 mol%     $x_2 = 0.6$      $p_{02} = 732$  mbar at 100 °C  
 Xylene : 10 mol%     $x_3 = 0.1$      $p_{03} = p_{0S} = 306$  mbar at 100 °C

Calculation of the bubble pressure:

$$P_{\text{boil}} = 0.3 * 1795 + 0.6 * 732 + 0.1 * 306 = 1008 \text{ mbar}$$

The bubble point lies at 100 °C and 1008 mbar total pressure.

What is the composition of the vapour?

$$\text{Benzene } y_1 = x_1 * \frac{p_{01}}{P_{\text{tot}}} = 0.3 * \frac{1795}{1008} = 0.534 \text{ molfr.}$$

$$\text{Toluene } y_2 = 0.6 * \frac{732}{1008} = 0.435 \text{ molfr.}$$

$$\text{Xylene } y_3 = 0.1 * \frac{306}{1008} = 0.031 \text{ molfr.}$$

**Cross-check calculation for the liquid composition  $x_1$  of benzene:**

$$x_1 = \frac{y_1 * P_{\text{tot}}}{P_{01}} = \frac{0.534 * 1008}{1795} = 0.3 \text{ molfr.}$$

**Alternative calculation of the vapour composition using the relative volatility  $\alpha$  based on the vapour pressure of the heaviest component xylene with  $P_{0h} = 306$  mbar:**

$$\begin{aligned}\alpha_1 &= \frac{1795}{306} = 5.87 & \alpha_2 &= \frac{732}{306} = 2.39 & \alpha_3 &= \frac{306}{306} = 1 \\ y_1 &= \frac{0.3 * 5.87}{0.3 * 5.87 + 0.6 * 2.39 + 0.1 * 1} = 0.534 \text{ molfr.} \\ y_2 &= \frac{0.6 * 2.39}{0.3 * 5.87 + 0.6 * 2.39 + 0.1 * 1} = 0.435 \text{ molfr.} \\ y_3 &= \frac{0.1 * 1}{0.3 * 5.87 + 0.6 * 2.39 + 0.1 * 1} = 0.031 \text{ molfr.}\end{aligned}$$

**Cross-check calculation for  $x_1$ :**

$$x_1 = \frac{y_1/\alpha_1}{\sum y/\alpha} = \frac{0.534/5.87}{0.534/5.87 + 0.435/2.39 + 0.031/1} = 0.3 \text{ molfr.}$$

**The calculation of the bubble and dew points follows using the equations from Sects. 2.3 and 2.4.**

The **bubble point** of a mixture is defined as follows:  $\sum y_i = \sum K_i * x_i = 1$

The **bubble pressure** can be calculated directly:  $P_{\text{boil}} = x_1 * p_{01} + x_2 * p_{02} + x_3 * p_{03}$

The **dew point** of a mixture is defined as follows:  $\sum x_i = \sum y_i/K_i = 1$

The **dew pressure** for the vapour composition  $z$  can be calculated directly:

$$\frac{1}{P_{\text{dew}}} = \frac{z_1}{p_{01}} + \frac{z_2}{p_{02}} + \frac{z_3}{p_{03}} + \frac{z_4}{p_{04}} \quad P_{\text{dew}} = \left[ \sum \frac{z_i}{p_{0i}} \right]^{-1}$$

**Example 2.9.2: Calculation of the bubble point for a four-component mixture  $C_{14}$ – $C_{17}$  at a pressure of 100 mbar.**

$$x_1 = 0.315 \quad x_2 = 0.276 \quad x_3 = 0.227 \quad x_4 = 0.182$$

The vapour pressures of the individual components are calculated.

The sum of the partial pressures  $\sum P_i$  is plotted against temperature.

Temperature (°C)	Vapour pressure (mbar)				$\sum x_i * p_{0i} = \sum P_i$
	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	
175	116.4	68.7	40.7	24.5	69.3 mbar
180	137.2	82.3	49.5	29.9	82.6 mbar
184	156.1	94.6	57.5	34.9	94.7 mbar
186	166.3	101.4	62	37.6	101.3 mbar

A bubble point temperature of 185.5 °C at 100 mbar is achieved by interpolation (Fig. 2.14).

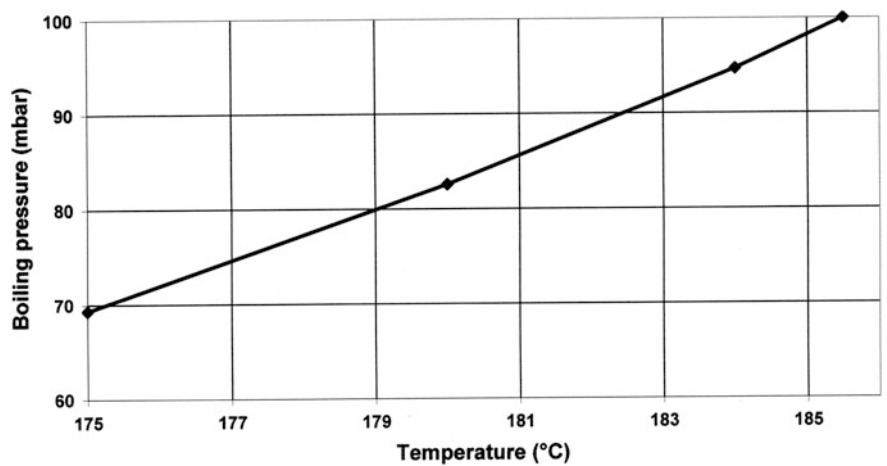


Fig. 2.14 Bubble point determination for the C<sub>14</sub>–C<sub>17</sub> mixture

**Example 2.9.3: Calculation of the dew point for a four-component C<sub>14</sub>–C<sub>17</sub> mixture at 100 mbar.**

Vapor composition :  $z_1 = 0.315$        $z_2 = 0.276$        $z_3 = 0.227$        $z_4 = 0.182$

The vapour pressures are calculated using the Antoine Constants.

The quotient  $\sum z_i/p_{0i}$  is calculated for different temperatures.

At total pressure  $P = 100$  mbar the dew point lies at the quotient  $\sum z_i/p_{0i} = 1/100 = 0.01$ .

Temperature (°C)	Vapor pressure (mbar)				$\sum z_i/p_{0i}$
	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	
200	255.0	160.2	101.3	62.7	0.0081
198	240.3	150.4	94.7	58.4	0.00866
196	226.4	141.1	88.4	54.4	0.00925
194	213.0	132.3	82.5	50.6	0.00985
192	200.5	123.9	76.9	47.1	0.0106

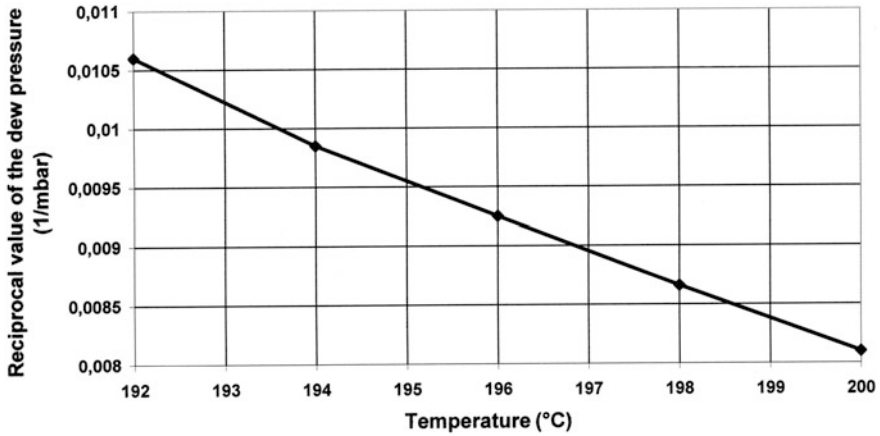


Fig. 2.15 Determination of the dew point temperature for a C<sub>14</sub>-C<sub>17</sub> mixture

A dew point temperature of 193.6 °C at 100 mbar is achieved by interpolation (Fig. 2.15).

## 2.10 Flash Calculations for Ideal Multi-component Mixtures [2]

For mixtures with more than two components the calculation must be performed iteratively. The individual  $V/F$  values of the different components are calculated with an estimate of  $V/F$ . The sum of the  $V/F$  values of the component must equal the  $V/F$  estimate.

$$\frac{V}{F} = \sum \frac{z_i}{1 + \frac{L}{V \cdot K_i}} \quad \frac{L}{V} = \frac{F}{V} - 1 = \frac{1}{V/L}$$

$$y_i = \frac{F}{V} * \left( \frac{z_i}{1 + \frac{L}{V \cdot K_i}} \right) \quad x_i = \frac{F}{V} * \left( \frac{z_i}{K_i + \frac{L}{V}} \right)$$

The following is required for the calculation: the vapour composition  $z_i$  of the individual components as mole fractions and the equilibrium constants  $K_i = p_{0i}/P_{\text{tot}}$ . The calculation is carried out iteratively with an estimate of  $V/F$  value.

$$\frac{L}{V} = \frac{F}{V} - 1$$



$V/F$  = molar ratio of the vapour rate  $V$  to the feed rate  $F$ .

$F/V$  = molar ratio of the feed rate  $F$  to the vapour rate  $V$ .

$L/V$  = molar ratio of the liquid rate  $L$  to the vapour rate  $V$ .

**Example 2.10.1: Calculation of the  $L/V$  ratio.**

$V/F = 0.5$  which means that 50% of the feed in kmol/h is vapour.

$$\frac{L}{V} = \frac{F}{V} - 1 = \frac{1}{0.5} - 1 = 1$$

**Example 2.10.2: Flash calculation for a four-component  $C_{14}$ – $C_{17}$  mixture.**

Pressure: 100 mbar

Temperature: 188 °C

**First estimate:  $V/F = 0.3$ ;  $L/F = 2.33$**

Component	$z_i$ (molfr.)	$P_{0i}$ (mbar)	$K_i$	$\frac{z_i}{1 + 2.33 \frac{1}{K_i}}$
C14	0.315	177	1.77	0.1359
C15	0.276	109	1.09	0.0879
C16	0.227	67	0.67	0.0507
C17	0.182	41	0.41	0.0272
				0.3017 = $V/F_i$

$\sum V/F_i = 0.3017 > V/F_{\text{chosen}} \rightarrow$  choose the higher value for  $V/F \rightarrow V/F = 0.32 \rightarrow L/V = 2.125$

Component	$z_i$ (molfr.)	$\frac{z_i}{1 + 2.125 \frac{1}{K_i}}$
C14	0.315	0.14315
C15	0.276	0.09357
C16	0.227	0.05442
C17	0.182	0.02944
		0.32058 = $V/F_i$

$\sum V/F_i > V/F_{\text{chosen}} \rightarrow$  choose the higher value for  $V/F \rightarrow V/F = 0.33 \rightarrow L/V = 2.03$

Component	$z_i$ (molfr.)	$\frac{z_i}{1 + 2.03 \frac{1}{K_i}}$
C14	0.315	0.14671
C15	0.276	0.09641
C16	0.227	0.05632
C17	0.182	0.03058
		0.33002 = $V/F_i$

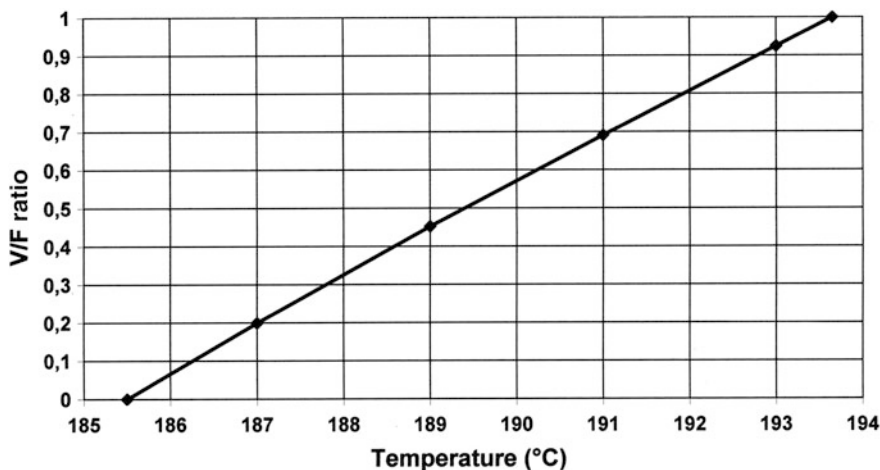


Fig. 2.16 Flash curve for the C<sub>14</sub>–C<sub>17</sub> mixture with a molar V/F ratio as a function of temperature

If the ratio  $\sum V_i/F_i < V/F \rightarrow$  choose the lower value of V/F!

If the ratio  $\sum V_i/F_i > V/F \rightarrow$  choose the higher value for V/F!

A deviation of 0.0005 is sufficiently accurate!

The flash curve for the C<sub>14</sub>–C<sub>17</sub> mixture is depicted in Fig. 2.16.

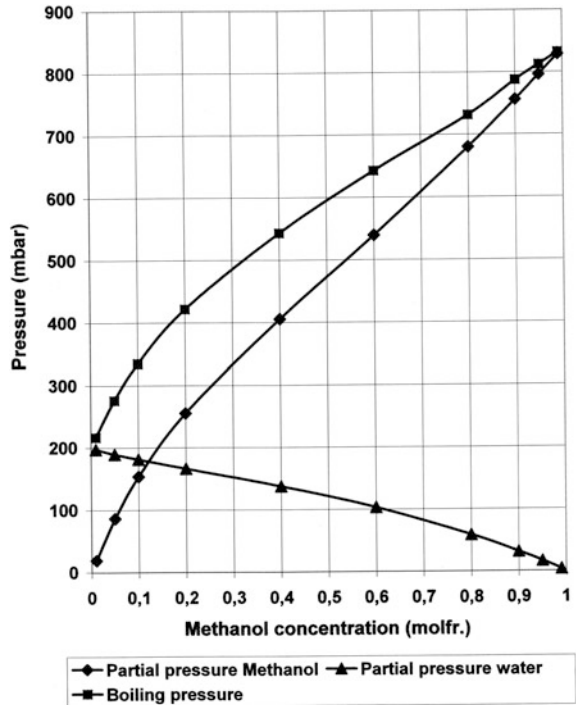
## 2.11 Phase Equilibrium of Non-ideal Binary Mixtures

With non-ideal mixtures the laws of Raoult and Dalton are invalid. The partial pressure lines are non-linear. Instead they curve upward or downward. Figure 2.17 shows the real partial pressures of methanol and water at 60 °C, considering the activity coefficient and also the total pressure resulting from the partial pressures as functions of the methanol composition.

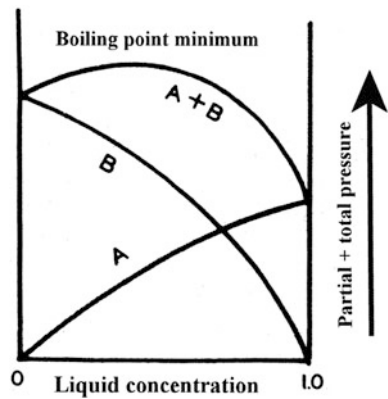
With the ideal calculation the curves are linear according to the laws of Raoult and Dalton. This is shown in Fig. 2.2. With the real calculation, considering the activity factor  $\gamma$  for the non-ideal behavior, the curves of partial pressure and total pressure curve upward. A higher total pressure and a lower bubble point temperature results for the mixture.

With azeotropic mixtures vapour pressure maxima and vapour pressure minima can occur. This is shown in Figs. 2.18 and 2.19 for a mixture from A and B. The calculation must be performed with a correction factor for the interaction of the partial pressures. This correction factor is termed the activity coefficient  $\gamma$ . The activity coefficient is dependent on the composition in the liquid phase and the temperature.

**Fig. 2.17** Partial pressure and total pressure for the non-ideal methanol–water mixture at 60 °C as function of methanol composition in the liquid

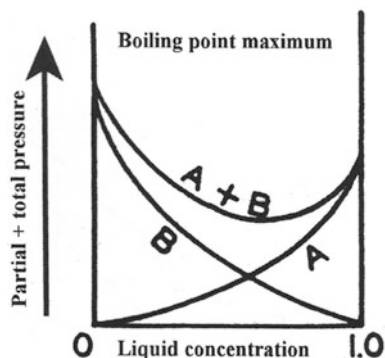


**Fig. 2.18** Partial pressures for A and B and total pressure A + B for an azeotropic mixture with a bubble point minimum



In the calculation of the equilibria for two-component and multi-component mixtures the interactions of the partial pressures are considered using the **activity coefficients**. Section 2.12 shows how the activity coefficient is calculated using different models. The following table of activity coefficients for methanol and water at 60 °C illuminates the influence of the composition on the activity coefficient.

**Fig. 2.19** Partial pressures for A and B and total pressure  $A + B$  for an azeotropic mixture with a bubble point maximum



Methanol composition (molfraction)	Activity coefficient of methanol	Activity coefficient of water
0.01	2.3069	1.002
0.05	2.0657	1.0035
0.1	1.8356	1.0131
0.2	1.5263	1.0462
0.4	1.2113	1.152
0.6	1.0737	1.2967
0.8	1.0153	1.4737
0.9	1.0035	1.5737
0.99	1.000	1.67

The correction of the partial pressures of the components of a mixture using the activity coefficient  $\gamma$  influences the vapour–liquid equilibrium as follow:

$$P_{\text{tot}} = \gamma_1 * x_1 * p_{01} + \gamma_2 * x_2 * p_{02} (\text{mbar})$$

$$y_1 * P_{\text{tot}} = \gamma_1 * x_1 * p_{01}$$

**Vapor composition:**

$$y_1 = \frac{x_1 * p_{01} * \gamma_1}{P_{\text{tot}}} \text{ (molfr.)}$$

$$y_2 = \frac{x_2 * p_{01} * \gamma_2}{P_{\text{tot}}} \text{ (molfr.)}$$

**Equilibrium constant:**

$$K_1 = \frac{p_{01} * \gamma_1}{P_{\text{tot}}}$$

$$K_2 = \frac{p_{02} * \gamma_2}{P_{\text{tot}}}$$

**Separation factor = Relative volatility  $\alpha$ :**

$$\alpha = \frac{K_1}{K_2} = \frac{\gamma_1 * P_{01}}{\gamma_2 * P_{02}}$$

$K_1$  = equilibrium factor for component 1

$K_2$  = equilibrium factor for component 2

$P_{\text{tot}}$  = total pressure in the system (mbar)

$p_{01}$  = vapour pressure of component 1 (mbar)

$p_{02}$  = vapour pressure of component 2 (mbar)

$x_1$  = liquid composition of component 1

$y_1$  = vapour composition of component 1

$x_2$  = liquid composition of component 2

$y_2$  = vapour composition of component 2

$\gamma_1$  = activity coefficient of component 1

$\gamma_2$  = activity coefficient of component 2

The activity coefficient  $\gamma$  is strongly dependent on composition and can be calculated using different models: Wilson, NRTL, Uniquac, and Unifac.

**Example 2.11.1: Non-ideal equilibrium for methanol–water**

Below is the equilibrium calculation for a methanol [1]–water [2] mixture at 92.1 °C and  $P_{\text{tot}} = 1000$  mbar.

Required data for calculation:

$$\begin{array}{ll} x_1 = 0.0535 & x_2 = 0.9465 \\ \gamma_1 = 1.848 & \gamma_2 = 1.004 \\ p_{01} = 2.817 \text{ mbar} & p_{02} = 756.4 \text{ mbar} \end{array}$$

$$y_1 = \frac{1.848 * 0.0535 * 2817}{1000} = 0.279$$

$$y_2 = \frac{1.004 * 0.9465 * 756.4}{1000} = 0.721$$

$$K_1 = \frac{1.848 * 2817}{1000} = 5.218 \quad K_2 = \frac{1.004 * 756.4}{1000} = 0.761$$

$$\alpha = \frac{K_1}{K_2} = \frac{5.218}{0.761} = 6.853$$

For comparison purposes **the ideal relative volatility**, without considering the activity coefficient, is calculated below:

$$\alpha_{\text{ideal}} = \frac{p_{01}}{p_{02}} = \frac{2.817}{756.4} = 3.724$$

**Conclusion: The influence of  $\gamma$  is substantial!** Due to the activity coefficient the separation factor is nearly doubled. The activity coefficient  $\gamma$  depends on the temperature and very strongly on the composition in the liquid phase.

**Example 2.11.2: Activity coefficient at different compositions.**

Influence of the composition on the activity coefficient of methanol [1] in water [2] at 30 °C.

$x_1$  = methanol composition in the liquid     $\gamma_1$  = activity coefficient of methanol

$x_1$	0.001	0.01	0.1	0.15	0.2
$\gamma_1$	2.596	2.521	1.968	1.765	1.609

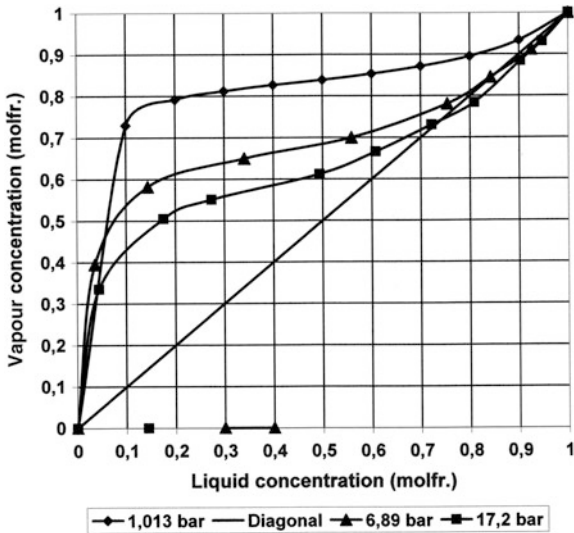
The dependency on the *temperature* is shown in the following table for  $x = 0.1$ .

Temperature	30 °C	60 °C	85 °C
$\gamma$ according to Wilson	1.968	1.836	1.744

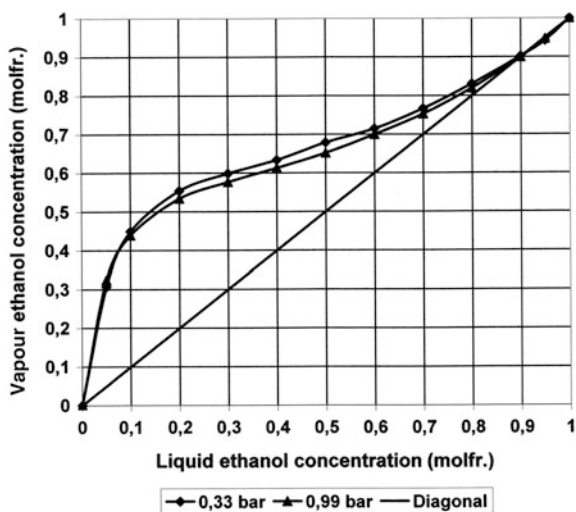
**Remark** At an azeotropic composition  $y = x$  and  $\alpha = 1$ . Thus it follows that  $\Rightarrow p_{01}/p_{02} = \gamma_2/\gamma_1$

An azeotropic point is reached if the activity coefficient in the diluted phase is greater than the vapour pressure ratio. In the following Figs. 2.20, 2.21, 2.22 and 2.23 some vapour–liquid equilibria of non-ideal mixtures are depicted. To illuminate the pressure dependency of the phase equilibrium the equilibria at different pressures are shown.

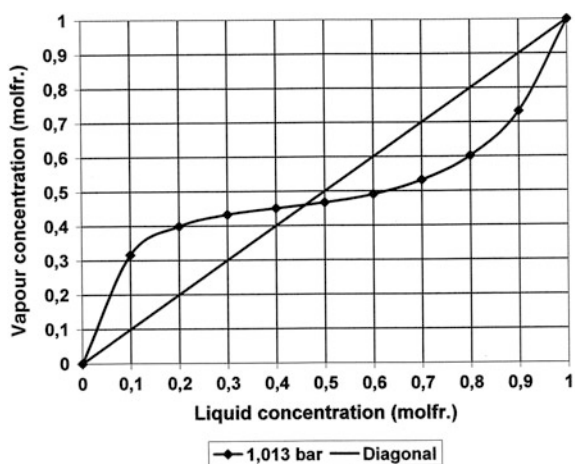
**Fig. 2.20** Vapour–liquid equilibrium of acetone–water at different pressures



**Fig. 2.21** Equilibrium of the azeotropic ethanol–water mixture at different pressures



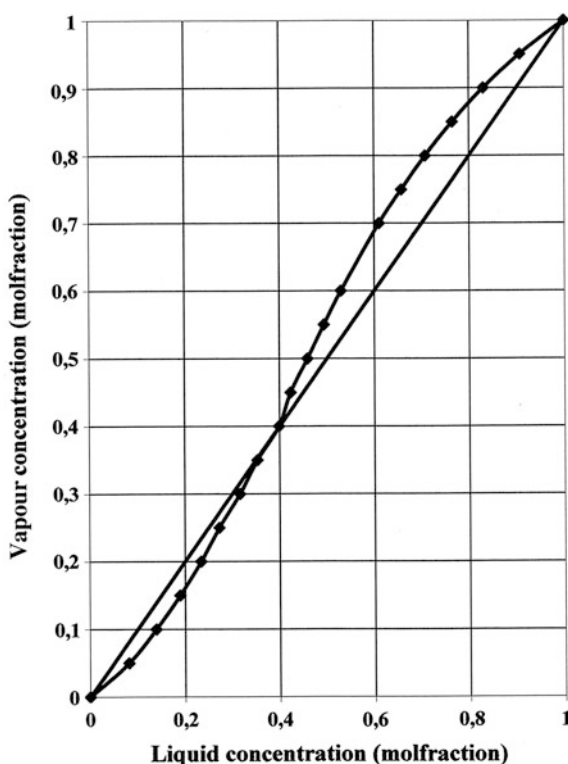
**Fig. 2.22** Equilibrium of the azeotropic ethanol–benzene mixture with a minimum bubble point



**Other examples for azeotropes with minimum bubble points are:**

Ethylacetate–ethanol  
 Isopropanol–water  
 Methanol–benzene  
 Water–butanol  
 Methanol–trichlorethylene  
 Sulphur carbon–acetone

**Fig. 2.23** Equilibrium of the azeotropic acetone–chloroform mixture at 1013 bar with a maximum bubble point



**Other examples of azeotropes with maximum bubble points are:**

Saltpetre acid–water

Water–formic acid

## 2.12 Calculation of the Activity Coefficients

The calculation of the activity coefficients using different models is described in the Refs. [3–6]. The required data for the calculations are given in [7]. In the following text the calculation of the activity coefficients using 3 models is shown. A fourth method is the **Unifac Model**, a group contribution method which does not require measured equilibrium data.



### 2.12.1 Calculation According to Wilson for Miscible Components [8]

$$\Lambda_{1,2} = \frac{V_2}{V_1} * \exp\left(\frac{\lambda_{12}}{R * T}\right)$$

$$\Lambda_{2,1} = \frac{V_1}{V_2} * \exp\left(\frac{\lambda_{12}}{R * T}\right)$$

$$\ln \gamma_1 = -\ln (X_1 + X_2 * \Lambda_{1,2}) + X_2 * \left[ \frac{\Lambda_{1,2}}{X_1 + X_2 * \Lambda_{1,2}} - \frac{\Lambda_{2,1}}{X_2 + X_1 * \Lambda_{2,1}} \right]$$

$$\ln \gamma_1^\infty = 1 - \ln \Lambda_{1,2} - \Lambda_{2,1}$$

**Required data:**

$\lambda_{12}$  and  $\lambda_{21}$  = interaction parameter.

$v_1$  and  $v_2$  = molar volume of the liquid.

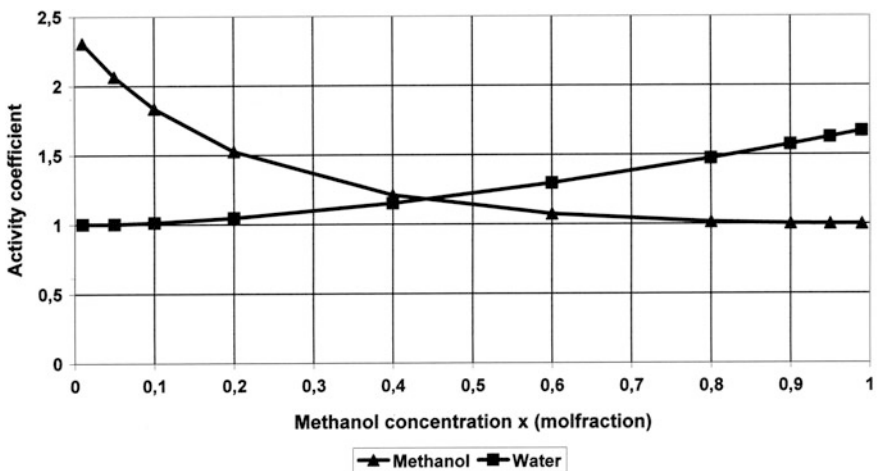
**Example 2.12.1: Methanol [1]–water [2] at 30 °C and  $x_1 = 0.1$ .**

$$\begin{aligned} \lambda_{12} &= -107.389 & v_1 &= 40.73 \\ \lambda_{21} &= 469.578 & v_2 &= 18.07 \end{aligned}$$

$$\Lambda_{1,2} = \frac{18.07}{40.73} * \exp\left(-\frac{-107.389}{1.987 * 303}\right) = 0.371$$

$$\Lambda_{2,1} = \frac{40.73}{18.07} * \exp\left(-\frac{469.578}{1.987 * 303}\right) = 1.033$$

$$\ln \gamma_1 = -\ln (0.1 + 0.371 * 0.9) + 0.9 * \left[ \frac{0.371}{0.1 + 0.371 * 0.9} - \frac{1.033}{1.033 * 0.1 + 0.9} \right]$$



**Fig. 2.24** Activity coefficients of methanol and water at 60 °C as a function of the methanol composition in the mixture

$$\ln \gamma_1 = 0.677 \Rightarrow \gamma_1 = 1.968$$

$$\ln \gamma^\infty = 1 - \ln 0.371 - 1.033 = 0.958 \quad \gamma^\infty = 2.607$$

$\gamma^\infty$  = activity coefficient at infinite dilution.

In Fig. 2.24 the activity coefficients of methanol and water at different compositions are shown.

**Example 2.12.2: Calculation of the vapour–liquid equilibrium at 75.7 °C.**

Methanol composition  $x_1 = 0.3909$

Water composition  $x_2 = 0.6091$

Methanol vapour pressure  $p_{01} = 1526.8$  mbar

Water vapour pressure  $p_{02} = 413.8$  mbar

$$\Lambda_{1,2} = 0.47525$$

$$\Lambda_{2,1} = 0.98356$$

$$P_{\text{tot}} = 1013 \text{ mbar}$$

Calculation of the activity coefficient  $\gamma_1$  of methanol:

$$\begin{aligned} \ln \gamma_1 &= -\ln(x_1 + x_2 * \Lambda_{1,2}) + x_2 * \left[ \frac{\Lambda_{1,2}}{x_1 + x_2 * \Lambda_{1,2}} - \frac{\Lambda_{2,1}}{x_2 + x_1 * \Lambda_{2,1}} \right] \\ \ln \gamma_1 &= -\ln(0.3909 + 0.6091 * 0.47525) \\ &+ 0.6091 * \left[ \frac{0.47525}{0.3909 + 0.6091 * 0.47525} - \frac{0.98356}{0.6091 + 0.3909 * 0.98356} \right] \\ \ln \gamma_1 &= 0.2076 \quad \gamma_1 = 1.231 \end{aligned}$$

Calculation of the activity coefficient  $\gamma_2$  of water:

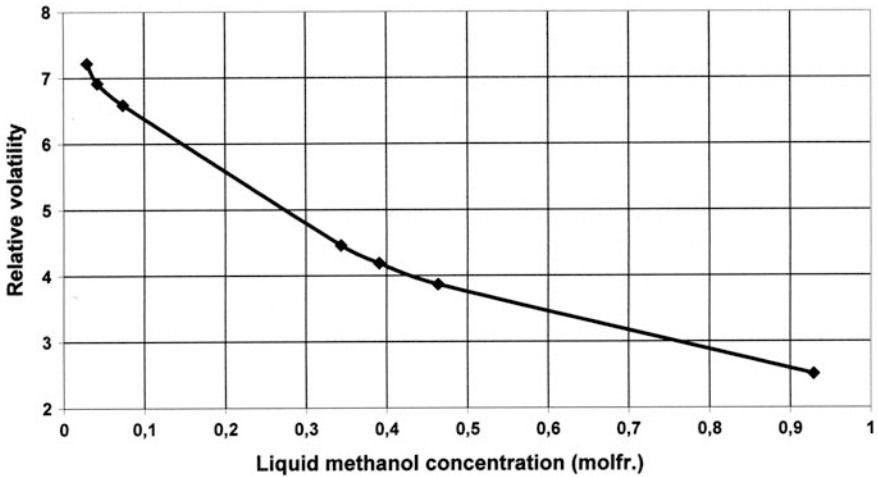
$$\begin{aligned} \ln \gamma_2 &= -\ln(x_2 + x_1 * \Lambda_{2,1}) - x_1 * \left[ \frac{\Lambda_{1,2}}{x_1 + x_2 * \Lambda_{1,2}} - \frac{\Lambda_{2,1}}{x_1 * \Lambda_{2,1} + x_2} \right] \\ \ln \gamma_2 &= -\ln(0.6091 + 0.3909 * 0.98356) \\ &- 0.3909 * \left[ \frac{0.47525}{0.3909 + 0.6091 * 0.47525} - \frac{0.98356}{0.6091 + 0.3909 * 0.98356} \right] \\ \ln \gamma_2 &= 0.120359 \quad \gamma_2 = 1.128 \end{aligned}$$

Calculation of the methanol composition  $y_1$  and the water composition  $y_2$  in the vapour:

$$\begin{aligned} y_1 &= \frac{x_1 * p_{01} * \gamma_1}{P_{\text{tot}}} = \frac{0.3909 * 1526.8 * 1.231}{1013} = 0.72 \text{ molfr.} \\ y_2 &= \frac{x_2 * p_{02} * \gamma_2}{P_{\text{tot}}} = \frac{0.6091 * 413.8 * 1.128}{1013} = 0.28 \text{ molfr.} \end{aligned}$$

Calculation of the vapour composition with relative volatility  $\alpha$ :

$$\begin{aligned} \alpha &= \frac{\gamma_1 * p_{01}}{\gamma_2 * p_{02}} = \frac{1.231 * 1526.8}{1.128 * 413.8} = 4.027 \\ y_1 &= \frac{\alpha_{1,2} * x_1}{1 + (\alpha_{1,2} - 1) * x_1} = \frac{4.027 * 0.3909}{1 + (4.027 - 1) * 0.3909} = 0.72 \end{aligned}$$



**Fig. 2.25** Relative volatility  $\alpha$  for methanol–water as function of the methanol composition in the liquid phase

From Fig. 2.25 it can be seen that the separation factor  $\alpha$  for the non-ideal mixture methanol–water decreases with increasing methanol composition.

### 2.12.2 Calculation According to NRTL for Partially Miscible Components with Two Liquid Phases [9]

$$\tau_{12} = \frac{g_{12}}{R * T} \quad \tau_{21} = \frac{g_{21}}{R * T}$$

$$G_{12} = \exp(-\alpha_{12} * \tau_{12}) \quad G_{21} = \exp(-\alpha_{21} * \tau_{21})$$

$$\ln \gamma_1 = X_2^2 * \left[ \tau_{21} * \left( \frac{G_{21}}{X_1 + X_2 + G_{21}} \right)^2 + \frac{\tau_{12} * G_{12}}{(X_2 + X_1 * G_{12})^2} \right]$$

$$\gamma^\infty = \tau_{21} + \tau_{12} * G_{12}$$

#### Required data:

$g_{12}$  and  $g_{21}$  = interaction parameter

$\alpha_{12} = \alpha_{21}$  = non-randomness factor

#### Example 2.12.2.1: Methanol [1]–water [2] at 30 °C and $x_1 = 0.1$ .

$$g_{12} = -253.965 \text{ cal/mol} \quad g_{21} = 845.16 \text{ cal/mol} \quad \alpha_{12} = 0.299$$

$$\tau_{12} = \frac{-253.965}{1.987 * 303} = -0.422 \quad \tau_{21} = \frac{845.16}{1.987 * 303} = 1.4$$

$$G_{12} = \exp(-0.299 * -0.422) = 1.134$$

$$G_{21} = \exp(-0.299 * 1.404) = 0.657$$

$$\ln \gamma_1 = 0.9^2 * \left[ 1.404 * \left( \frac{0.657}{0.1 + 0.9 * 0.657} \right)^2 + \frac{-0.422 * 1.134}{(0.9 + 0.1 * 1.134)^2} \right]$$

$$\ln \gamma_1 = 0.65 \Rightarrow \gamma_1 = 1.915$$

$$\ln \gamma_1^\infty = 1.404 + (-0.422) * 1.134 = 0.925 \Rightarrow \gamma_1^\infty = 2.522$$

### 2.12.3 Calculation According to Uniquac for Components with a Miscibility Gap

$$\tau_{12} = \exp\left(-\frac{u_{12}}{R * T}\right) \quad \tau_{21} = \exp\left(-\frac{u_{21}}{R * T}\right)$$

$$\varphi_i = \frac{r_i * x_i}{\sum r_i * x_i} \quad \vartheta_i = \frac{q_i * x_i}{\sum q_i * x_i}$$

$$l_i = \frac{z}{2} * (r_i - q_i) - (r_i - 1)$$

$$\ln \gamma_1 = \ln \gamma_{1C} + \ln \gamma_{1R}$$

$$\ln \gamma_{1C} = \ln \frac{\varphi_1}{x_1} + \frac{z}{2} * q_1 * \ln \frac{\vartheta_1}{\varphi_1} + \varphi_2 * (l_1 - \frac{r_1}{r_2} * l_2)$$

$$\ln \gamma_{1R} = -q_1 * \ln(\vartheta_1 + \tau_{21} * \vartheta_2)$$

$$+ \vartheta_2 * q_1 * \left( \frac{\tau_{21}}{\vartheta_1 + \tau_{21} * \vartheta_2} - \frac{\tau_{12}}{\vartheta_2 + \tau_{12} * \vartheta_1} \right)$$

#### Required data:

$u_{12}$  and  $u_{21}$  = interaction parameters.

$r$  = volume parameter (van der Waals).

$q$  = surface parameter (van der Waals).

$z$  = coordination number (mostly = 10).

**Example 2.12.3.1: Calculation of activity coefficient of methanol in a methanol–water mixture at 30 °C.**

$$u_{12} = -328.451 \text{ cal/mol} \quad u_{21} = 506.088 \text{ cal/mol}$$

$$r_1 = 1.4311 \quad r_2 = 0.92$$

$$q_1 = 1.432 \quad q_2 = 1.40$$

Methanol composition  $x_{\text{Meth}} = 0.1$  molfr. = 10 mol%

$$\varphi_1 = \frac{0.1 * 1.4311}{0.1 * 1.4311 + 0.9 * 0.92} = 0.147$$

$$\varphi_2 = 1 - 0.1473 = 0.853$$

$$\vartheta_1 = \frac{0.1 * 1.432}{0.1 * 1.432 + 0.9 * 1.4} = 0.102$$

$$\vartheta_2 = 1 - 0.102 = 0.898$$

$$l_1 = 10/2 * (1.4311 - 1.432) - (1.4311 - 1) = -0.4356$$

$$l_2 = 10/2 * (0.92 - 1.40) - (0.92 - 1) = -2.32$$

$$\tau_{12} = \exp\left(-\frac{-328.451}{1.987 * 303}\right) = 1.7255$$

$$\tau_{12} = \exp\left(-\frac{506.088}{1.987 * 303}\right) = 0.4314$$

$$\begin{aligned} \ln \gamma_{1C} = & \ln \frac{0.147}{0.1} + \frac{10}{2} * 1.4311 * \ln \frac{0.102}{0.147} \\ & + 0.853 * \left[ -0.4356 - \frac{1.4311}{0.92} * (-2.32) \right] = 0.471 \end{aligned}$$

$$\begin{aligned} \ln \gamma_{1R} = & -1.432 * \ln (0.102 + 0.4314 * 0.898) + 0.898 * 1.432 \\ & * \left( \frac{0.4314}{0.102 + 0.898 * 0.4314} - \frac{1.7255}{0.898 + 0.102 * 1.7255} \right) = 0.0908 \end{aligned}$$

$$\ln \gamma_1 = 0.477 + 0.0908 = 0.5678 \Rightarrow \gamma_1 = \mathbf{1.764}$$

#### 2.12.4 Critical Comparison of the Activity Coefficients Calculated Using Different Models

The available models for equilibria calculations of distillation and absorption plants or the design of condensers and evaporators can be simplified with the use of computer. Substantial discrepancies can be seen if the results of the different calculation methods are compared. This is shown in the following Examples 2.12.4.1 and 2.12.4.2.

##### Example 2.12.4.1: Activity coefficients for a pentane–toluene mixture.

Composition: 10 mol% Pentane, 90 mol% Toluene

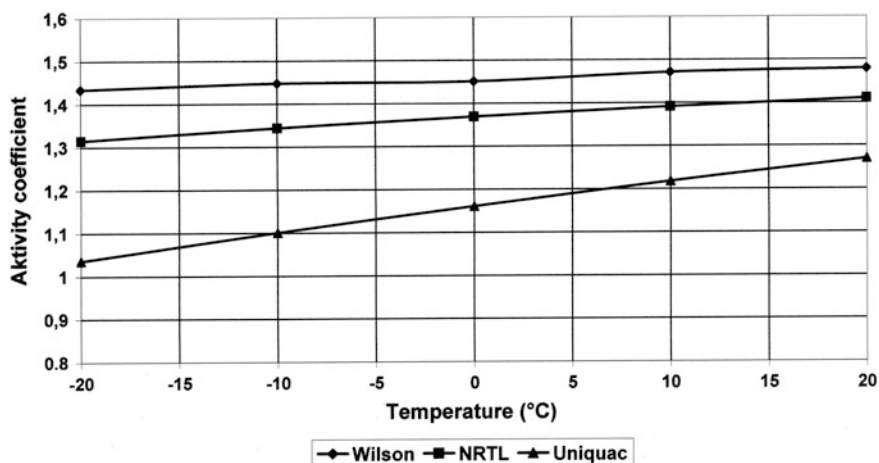


Fig. 2.26 Activity coefficient of pentane in toluene as function of temperature, using different models

### Interaction parameters:

Wilson:	$\lambda_{11} = 0$	$\lambda_{12} = -296.9388$	$\lambda_{21} = 1145.5506$	$\lambda_{22} = 0$	
NRTL	$g_{11} = 0$	$g_{12} = 1401.7145$	$g_{21} = -490.4151$	$g_{22} = 0$	$\alpha = 0.298$
Uniquac	$u_{11} = 0$	$u_{12} = 869.1587$	$u_{21} = -436.4687$	$u_{22} = 0$	

**Conclusion:** The activity coefficients calculated using different models for pentane in toluene deviate considerably (Fig. 2.26). The activity coefficient of pentane becomes greater with increasing temperature. Additionally the non-temperature dependent activity coefficients of pentane are calculated according to Margules and van Laar.

Margules:  $\gamma = 1.44$  for Pentane.

van Laar:  $\gamma = 1.47$  for Pentane.

The activity coefficient of toluene lies constantly at 1.

### Example 2.12.4.2: Activity coefficients for the a hexane, ethyl acetate, and toluene mixture

#### Composition:

Hexane:  $x = 0.3 = 30$  mol%.

Ethyl acetate:  $x = 0.3 = 30$  mol%.

Toluene:  $x = 0.4 = 40$  mol%.

Interaction parameter	Wilson	Uniquac	NRTL	Alpha
1/1	0	0	0	0
1/2	107.1217	302.7052	427.6309	0.2995
1/3	21.0210	112.6399	130.3146	0.3016
2/1	618.7792	-83.8122	255.6205	0.2995
2/2	0	0	0	0
2/3	135.1766	-62.3228	63.3896	0.3021
3/1	246.4956	-57.7374	131.5420	0.3016
3/2	15.6079	63.3994	86.1714	0.3021
3/3	0	0	0	0

### Calculation results:

	Wilson		Uniquac		NRTL	
	20 °C	30 °C	20 °C	30 °C	20 °C	30 °C
Hexane	1.373	1.36	1.37	1.358	1.376	1.363
Ethyl acetate	1.264	1.257	1.251	1.246	1.269	1.26
Toluene	1.031	1.03	1.017	1.018	1.029	1.028

The deviations range 0.2–1%!

## 2.13 Bubble Point, Dew Point, and Flash Separation for Non-ideal Binary Mixtures

For non-ideal mixtures the influence of the activity coefficient  $\gamma$  must be considered in the calculation of the partial pressure.

**Example 2.13.1: Bubble point calculation with the activity coefficient for the methanol [1]–water [2] mixture.**

$$\begin{aligned}
 x_1 &= 0.1 & x_2 &= 0.9 & t &= 87.8\text{ °C} & P_{\text{tot}} &= 1000\text{ mbar} \\
 \gamma_1 &= 1.705 & \gamma_2 &= 1 \\
 p_{01} &= 2438\text{ mbar} & p_{02} &= 646\text{ mbar}
 \end{aligned}$$

$$P_{\text{boil}} = x_1 * \gamma_1 * p_{01} + x_2 * \gamma_2 * p_{02} = 0.1 * 1.705 * 2438 + 0.9 * 1 * 646 = 997\text{ mbar} \approx 1\text{ bar}$$

**Cross-check calculation of the bubble point:**

$$K_1 = \frac{\gamma_1 * p_{01}}{P_{\text{tot}}} = \frac{1.705 * 2438}{1000} = 4.167 \qquad K_2 = \frac{1 * 646}{1000} = 0.64$$

$$\Sigma K_i * x_i = 0.1 * 4.167 + 0.9 * 0.64 = 1$$

Therefore, the bubble point condition is fulfilled at 87.8 °C!

Without considering the activity coefficient  $\gamma$  a bubble point temperature of 93.1 °C rather than one of 87.8 °C is obtained.

**Example 2.13.2: Dew point calculation with the activity coefficient  $\gamma$  for the methanol [1]-water [2] mixture.**

$$\begin{array}{lll} y_1 = 0.1 & y_2 = 0.9 & t = 97.1 \text{ °C} \quad P_{\text{tot}} = 1.000 \text{ mbar} \\ \gamma_1 = 2.2 & \gamma_2 = 1.0 & \\ p_{01} = 3.343 \text{ mbar} & p_{02} = 910.3 \text{ mbar} & \end{array}$$

$$\frac{1}{P_{\text{dew}}} = \frac{y_1}{\gamma_1 * p_{01}} + \frac{y_2}{\gamma_2 * p_{02}} = \frac{0.1}{2.2 * 3343} + \frac{0.9}{910.3} = 0.001 \quad P_{\text{dew}} = 1 \text{ bar}$$

**Cross-check calculation of the dew point:**

$$\begin{aligned} K_1 &= \frac{2.2 * 3343}{1000} = 7.373 & K_2 &= \frac{1 * 910.3}{1000} = 0.9125 \\ \sum \frac{y_i}{K_i} &= \frac{0.1}{7.373} + \frac{0.9}{0.9125} = 1 \end{aligned}$$

Therefore, the dew point condition is fulfilled at 97.1 °C!

**Example 2.13.3: Flash calculation for the methanol [1]-water [2] mixture**

$$\begin{array}{lll} P_{\text{tot}} = 1 \text{ bar} = 1000 \text{ mbar} & t = 92.1 \text{ °C} & \text{Feed rate} = 100 \text{ kmol/h} \\ \text{Feed compositions:} & z_1 = 0.1 \text{ molfr.} & z_2 = 0.9 \text{ molfr.} \\ & \gamma_1 = 1.848 & \gamma_2 = 1.004 \\ & p_{01} = 2823.7 \text{ mbar} & p_{02} = 758.3 \text{ mbar} \end{array}$$

$$\begin{aligned} K_1 &= \frac{1.848 * 2823.7}{1000} = 5.218 & K_2 &= \frac{1.004 * 758.3}{1000} = 0.7614 \\ \frac{V}{F} &= \frac{z_1 * \frac{K_1 - K_2}{1 - K_2} - 1}{K_1 - 1} = \frac{0.1 * \frac{5.218 - 0.7614}{1 - 0.7614} - 1}{5.218 - 1} = 0.2058 \end{aligned}$$

**At 92.1 °C 20.58% of the feed is vapour.**

Vapour rate  $V = 0.2058 * 100 = 20.58 \text{ kmol/h}$

Liquid rate  $L = 100 - 20.58 = 79.42 \text{ kmol/h}$

**Composition calculation in the liquid and the vapour:**

$$\begin{aligned} x_1 &= \frac{1 - K_2}{K_1 - K_2} = \frac{1 - 0.7614}{5.218 - 0.7614} = 0.0535 \text{ molfr.} \\ x_2 &= 1 - 0.0535 = 0.9465 (\text{molfr.}) = 94.65 \text{ mol\%} \end{aligned}$$

$$y_1 = K_1 * x_1 = 5.218 * 0.0535 = 0.279 \text{ molfr.} = 27.9 \text{ mol\%}$$

$$y_2 = K_2 * x_2 = 0.7614 * 0.9465 = 0.721 \text{ molfr.} = 72.1 \text{ mol\%}$$



Without consideration being given to the activity coefficient  $\gamma$ , the following incorrect results at 92.1 °C are obtained:

$$\begin{aligned} K_1 &= 2.74 & K_2 &= 0.758 \\ V &= 0 & L &= 100 \text{ kmol/h} \end{aligned}$$

Nothing is vaporized because the bubble point lies with  $\gamma = 1$  at 93.1 °C above 92.1 °C.

## 2.14 Non-ideal Multi-component Mixtures

The equilibria calculation of mixtures with more than two components is very complex and therefore done using computers. The compositions, the temperature, and the Antoine Constants for the vapour pressure and the interaction parameters for the equilibrium must be input. The activity coefficients are strongly dependent on the composition of the liquid phase. Example 2.14.1 shows how strongly the activity coefficient of water increases with decreasing water composition in the liquid phase.

**Example 2.14.1: Activity coefficient of water at different compositions.**

		Activity coefficient $\gamma$	
	$x$ (molfr.)	30 °C	50 °C
<i>n</i> -Heptane	0.2	1.1	1.014
Methyl ethyl ketone	0.2	1.138	1.13
Ethyl acetate	0.2	1.14	1.142
Toluene	0.2	1.63	1.606
Water	0.2	4.287	4.22

		Activity coefficient $\gamma$	
	$x$ (molfr.)	30 °C	50 °C
<i>n</i> -Heptane	0.225	1.138	1.128
Methyl ethyl ketone	0.225	1.088	1.087
Ethyl acetate	0.225	1.102	1.104
Toluene	0.225	1.338	1.323
Water	0.1	6.055	5.912

		Activity coefficient $\gamma$	
	$x$ (molfr.)	30 °C	50 °C
<i>n</i> -Heptane	0.2475	1.262	1.243
Methyl ethyl ketone	0.2475	1.066	1.07
Ethyl acetate	0.2475	1.096	1.098
Toluene	0.2475	1.133	1.125
Water	0.01	8.912	8.578

**Example 2.14.2: Flash calculation for a four-component mixture with different compositions at 1 bar total pressure as function of temperature.**

Mixture 1	$x$ (molfr.)	Activity coefficient
<i>n</i> -Heptane	0.25	1.65
Methyl ethyl ketone	0.25	1.331
Ethyl acetate	0.25	1.273
Toluene	0.25	0.974
Mixture 2	$x$ (molfr.)	Activity coefficient
<i>n</i> -Heptane	0.1	1.83
Methyl ethyl ketone	0.1	1.314
Ethyl acetate	0.4	1.112
Toluene	0.4	1.013

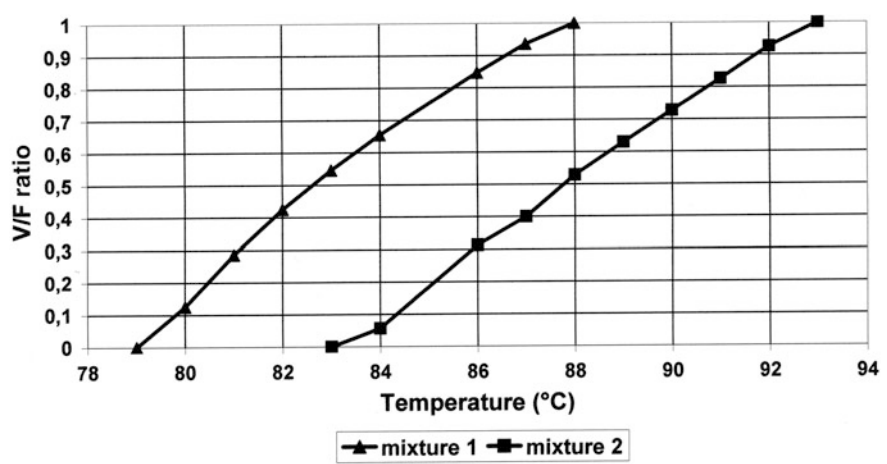
In Fig. 2.27 the flash curves for both of the different compositions are shown. Figure 2.28 shows how the composition of a non-ideal mixture of *n*-heptane, methyl ethyl ketone, ethyl acetate, and toluene changes in nine consecutive vaporization stages. After four vaporization stages the compositions scarcely change. If toluene is distilled off then the composition of the mixture remains constant:

Ethyl acetate:            45.7 mol%

Methyl ethyl ketone:    37.5 mol%

*n*-Heptane:                16.8 mol%

The composition curves in Fig. 2.28 result from Fig. 2.29 with the equilibrium constants *K* of the different components. After four vaporization stages the toluene has vanished and the *K* values lie at 1. At *K* = 1 the vapour composition *y* equals the liquid composition *x*. This is a ternary azeotropic mixture.



**Fig. 2.27** Flash curves for two non-ideal mixtures as a function of temperature

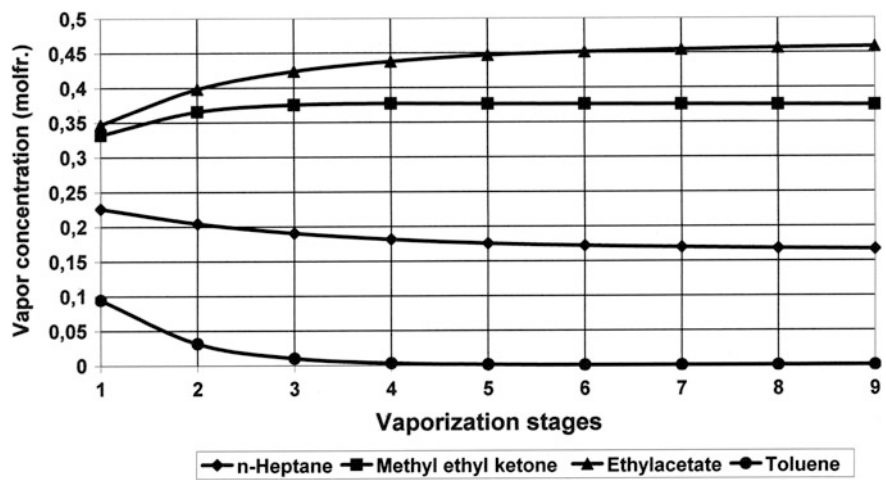


Fig. 2.28 The behaviour of the compositions of the four components with increasing number of vaporization stages

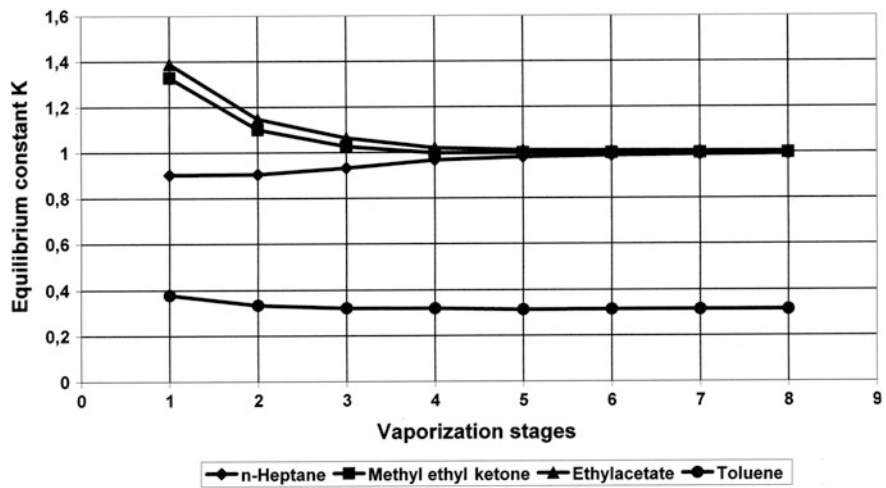


Fig. 2.29 Equilibrium constants of the components as a function of the vaporization stages

Although the three light components have different vapour pressures the separation factor  $\alpha$  is set to 1 by the activity coefficient.

The determining factor for the separation is the relative volatility.

	Bubble point (°C)	Mole weight
Ethyl acetate	77	88
Methyl ethyl ketone	80	72
Heptane	98.4	100
Toluene	110.6	92

**Example 2.14.3: Calculation of the relative volatility  $\alpha$  at 73 °C and  $P_{\text{tot}} = 977 \text{ mbar}$ .**

		$p_0 \text{ (mbar)}$	$p_0/P_{\text{tot}}$	$\gamma$	$K$
1.	<i>n</i> -Heptane	448.7	0.459	2.155	0.99
2.	Methyl ethyl ketone	800.5	0.827	1.206	0.998
3.	Ethyl acetate	878.8	0.899	1.117	1.005
4.	Toluene	302.4	0.309	1.017	0.315

$$\alpha_{1/2} = \frac{\gamma_1 * P_{01}}{\gamma_2 * P_{02}} = \frac{2.155 * 448.7}{1.206 * 800.5} = 1$$

$$\alpha_{2/3} = \frac{\gamma_2 * P_{02}}{\gamma_3 * P_{03}} = \frac{1.206 * 800.5}{1.117 * 878.8} = 0.98$$

$$\alpha_{1/3} = \frac{\gamma_1 * P_{01}}{\gamma_3 * P_{03}} = \frac{2.155 * 448.7}{1.117 * 878.8} = 0.985$$

$$\alpha_{3/4} = \frac{\gamma_3 * P_{03}}{\gamma_4 * P_{04}} = \frac{1.117 * 878.8}{1.017 * 302.4} = 3.19$$

$$\alpha_{1/4} = \frac{\gamma_1 * P_{01}}{\gamma_4 * P_{04}} = \frac{2.155 * 448.7}{1.017 * 302.4} = 3.19$$

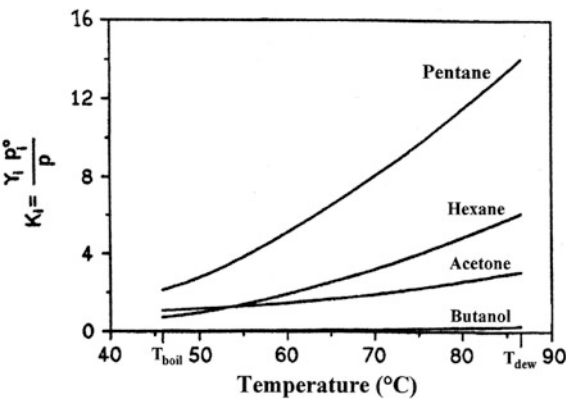
$$\alpha_{3/4} = \frac{\gamma_2 * P_{02}}{\gamma_4 * P_{04}} = \frac{1.206 * 800.5}{1.017 * 302.4} = 3.19$$

**Conclusion**

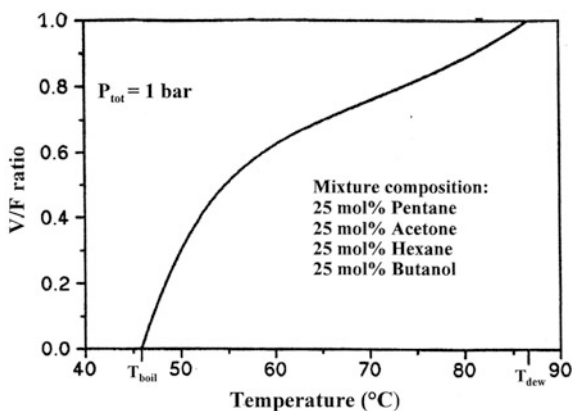
The first three components with a separation factor  $\alpha = 1$  do not allow separation. However, toluene with a separation factor  $\alpha = 3.19$  allows very simple separation.

Figures 2.30 and 2.31 show the calculation results for another non-ideal four-component mixture with non-ideal behaviour.

**Fig. 2.30** Equilibrium factors  $K$  for the different components of the mixture dependent of the temperature



**Fig. 2.31** Flash curve for the non-ideal, four-component mixture as function of temperature



## References

1. E.J. Henley, J.D. Seader, *Equilibrium Stage Separations in Chemical Engineering* (Wiley, New York, 1981)
2. B.D. Smith, *Design of Equilibrium Stage Processes* (McGraw-Hill, New York, 1963)
3. J. Gmehling, B. Kolbe, *Thermodynamik* (Georg Thieme Verlag, Stuttgart, 1988)
4. J.M. Prausnitz, J. Gmehling, *Thermische Verfahrenstechnik Phasengleichgewichte* (vt-Hochschulkurs III, Krausskopf-Verlag Mainz, 1980)
5. J. Gmehling, B. Kolbe, M. Kleiber, J. Rarey, *Chemical Thermodynamics for Process Simulation* (Wiley-VCH Verlag, Weinheim, 2012)
6. G. Mehos, Estimate binary equilibrium coefficients. *Chem. Eng.* **101** (1996)
7. J. Gmehling, U. Onken, Vapor-Liquid Equilibrium Data Collection, in DECHEMA-Chemistry Data Series ab (1977)
8. M. Hirata, Sh. Ohe, K. Nagahama, *Vapor-Liquid Equilibria* (Elsevier, New York, 1975)
9. H. R. Null, *Phase Equilibrium in Process Design* (Wiley-Interscience, New York, 1970)

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Nitsche, M.; Gbadamosi, R.O.

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