of state for both phases (for example, the SRK equation), and the VLE-condition $\mu_{g,i} = \mu_{l,i}$ gives

$$\phi_i^V y_i = \phi_i^L x_i \tag{7.44}$$

where the fugacity coefficients ϕ_i^V and ϕ_i^L are determined from the equation of state. The K value is then $K_i = \phi_i^L/\phi_i^V$. Note that (7.44) can also be used for supercritical components.

7.5 Flash calculations

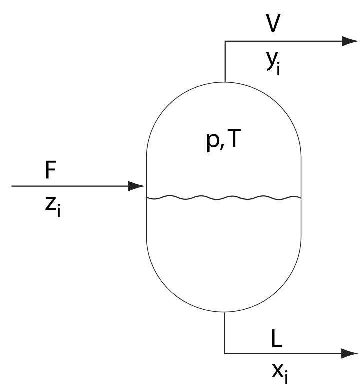

Figure 7.4: Flash tank

Flash calculations are used for processes with vapor/liquid-equilibrium (VLE). A typical process that requires flash calculations, is when a feed stream (F) is separated into a vapor (V) and liquid (L) product; see Figure 7.4.

In principle, flash calculations are straightforward and involve combining the VLE-equations with the component mass balances, and in some cases the energy balance. Some flash calculations are (with a comment on their typical numerical solution or usage):

1. Bubble point at given T (easy)
2. Bubble point at given p (need to iterate on T)
3. Dew point at given T (easy)
4. Dew point at given p (need to iterate on T)
5. Flash at given p and T (relatively easy)
6. Flash at given p and H ("standard" flash, e.g., for a flash tank after a valve)
7. Flash at given p and S (e.g., for condensing turbine)
8. Flash at given U and V (e.g., for dynamic simulation of an adiabatic flash drum)

The last three flashes are a bit more complicated as they require the use of the energy balance and relationships for computing H, S, etc. The use of flash calculations is best illustrated by some examples. Here, we assume that the VLE is given on K-value form, that is,

$$y_i = K_i x_i$$

Table 7.2: Data for flash examples and exercises: Antoine parameters for $p^{\text{sat}}(T)$, normal boiling temperature (T_b) and heat of vaporization $\Delta_{\text{vap}}H(T_b)$ for selected components. **Data**: Poling, Prausnitz and O'Connell, *The properties of gases and liquids*, 5th Ed., McGraw-Hill (2001).

```
% log10(psat[bar])=A-B/(T[K]+C)          Tb[K]         dvapHb [J/mol]
A1=3.97786;    B1=1064.840;  C1=-41.136;  Tb1=309.22;  dvapHb1=25790;  % pentane  C5H12
A2=4.00139;    B2=1170.875;  C2=-48.833;  Tb2=341.88;  dvapHb2=28850;  % hexane   C6H14
A3=3.93002;    B3=1182.774;  C3=-52.532;  Tb3=353.93;  dvapHb3=29970;  % cyclohex C6H12
A4=5.20277;    B4=1580.080;  C4=-33.650;  Tb4=337.69;  dvapHb4=35210;  % methanol CH3OH
A5=5.11564;    B5=1687.537;  C5=-42.98;   Tb5=373.15;  dvapHb5=40660;  % water    H2O
A6=4.48540;    B6= 926.132;  C6=-32.98;   Tb6=239.82;  dvapHb6=23350;  % ammonia  NH3
A7=3.92828;    B7= 803.997;  C7=-26.11;   Tb7=231.02;  dvapHb7=19040;  % propane  C3H8
A8=4.05075;    B8=1356.360;  C8=-63.515;  Tb8=398.82;  dvapHb8=34410;  % octane   C8H18
A9=4.12285;    B9=1639.270;  C9=-91.310;  Tb9=489.48;  dvapHb9=43400;  % dodecane C12H26
A10=3.98523; B10=1184.24;  C10=-55.578; Tb10=353.24; dvapHb11=30720;  % benzene  C6H6
A11=4.05043; B11=1327.62;  C11=-55.525; Tb11=383.79; dvapHb11=33180;  % toluene  C7H8
```

where y_i is the vapor phase mole fraction and x_i the liquid phase mole fraction for component i. In general, the "K-value" K_i depends on temperature T, pressure p and composition (both x_i and y_i). We mostly assume ideal mixtures, and use Raoult's law. In this case K_i depends on T and p only:

$$\text{Raoult's law}: \quad K_i = p_i^{\text{sat}}(T)/p$$

In the examples, we compute the vapor pressure $p^{\text{sat}}(T)$ using the Antoine parameters given in Table 7.2.

7.5.1 Bubble point calculations

Let us first consider bubble point calculations, In this case the liquid-phase composition x_i is given (it corresponds to the case where V is very small ($V \gtrsim 0$) and $x_i = z_i$ in Figure 7.4). *The bubble point of a liquid is the point where the liquid just starts to evaporate (boil)*, that is, when the first vapor bubble is formed. If the temperature is given, then we must lower the pressure until the first bubble is formed. If the pressure is given, then we must increase the temperature until the first bubble is formed. In both cases, this corresponds to adjusting T or p until the computed sum of vapor fractions is just 1, $\Sigma y_i = 1$ or

$$\Sigma_i K_i x_i = 1 \tag{7.45}$$

where x_i is given. For the ideal case where Raoult's law holds this gives

$$\Sigma_i \underbrace{x_i p_i^{\text{sat}}(T)}_{p_i} = p \tag{7.46}$$

Example 7.17 Bubble point at given temperature T. *A liquid mixture contains 50% pentane (1), 30% hexane (2) and 20% cyclohexane (3) (all in mol-%), i.e.,*

$$x_1 = 0.5; \quad x_2 = 0.3; \quad x_3 = 0.2$$

At $T = 400$ K, the pressure is gradually decreased. What is the bubble pressure and composition of the first vapor that is formed? Assume ideal liquid mixture and ideal gas (Raoult's law).

Solution. *The task is to find a p that satisfies (7.46). Since T is given, this is trivial; we can simply calculate p from (7.46). We start by computing the vapor pressures for the three components at $T = 400K$. Using the Antoine data in Table 7.2, we get:*

$$p_1^{\text{sat}}(400K) = 10.248 \text{ bar}$$

$$p_2^{\text{sat}}(400K) = 4.647 \text{ bar}$$
$$p_3^{\text{sat}}(400K) = 3.358 \text{ bar}$$

At the bubble point, the liquid phase composition is given, so the partial pressure of each component is

$$p_1 = x_1 p_1^{\text{sat}} = 5.124 \text{ bar}$$
$$p_2 = x_2 p_2^{\text{sat}} = 1.394 \text{ bar}$$
$$p_3 = x_3 p_3^{\text{sat}} = 0.672 \text{ bar}$$

Thus, from (7.46) the bubble pressure is

$$p = p_1 + p_2 + p_3 = 7.189 \text{ bar}$$

Finally, the vapor composition (composition of the first vapor bubble) is

$$y_1 = \frac{p_1}{p} = 0.713; \quad y_2 = \frac{p_2}{p} = 0.194; \quad y_3 = \frac{p_3}{p} = 0.093$$

For calculation details see the MATLAB code:

```
T=400; x1=0.5; x2=0.3; x3=0.2
psat1=10^(A1-B1/(T+C1)), psat2=10^(A2-B2/(T+C2)), psat3=10^(A3-B3/(T+C3))
p1=x1*psat1, p2=x2*psat2, p3=x3*psat3, p=p1+p2+p3
y1=p1/p, y2=p2/p, y3=p3/p
```

Example 7.18 Bubble point at given pressure p**.** *Consider the same liquid mixture with 50% pentane (1), 30% hexane (2) and 20% cyclohexane (3) (all in mol-%). A $p = 5$ bar, the temperature is gradually increased. What is the bubble temperature and composition of the first vapor that is formed?*

Solution. *In this case, p and x_i are given, and (7.46) provides an implicit equation for T which needs to be solved numerically, for example, by iteration. A straightforward approach is to use the method from the previous example, and iterate on T until the bubble pressure is 5 bar (for example, using the MATLAB code below). We find $T = 382.64$ K, and*

$$y_1 = \frac{p_1}{p} = 0.724; \quad y_2 = \frac{p_2}{p} = 0.187; \quad y_3 = \frac{p_3}{p} = 0.089$$

```
% MATLAB:
x1=0.5; x2=0.3; x3=0.2; p=5;
T=fzero(@(T) p-x1*10^(A1-B1/(T+C1))-x2*10^(A2-B2/(T+C2))-x3*10^(A3-B3/(T+C3)) , 400)
```

7.5.2 Dew point calculations

Let us next consider **dew point** calculations. In this case the vapor-phase composition y_i is given (it corresponds to the case where L is very small ($L \gtrsim 0$) and $y_i = z_i$ in Figure 7.4). The dew point of a vapor (gas) is the point where the vapor just begins to condense, that is, when the first liquid drop is formed. If the temperature is given, then we must increase the pressure until the first liquid is formed. If the pressure is given, then we must decrease the temperature until the first liquid is formed. In both cases, this corresponds to adjusting T or p until $\Sigma x_i = 1$ or

$$\Sigma_i y_i / K_i = 1 \tag{7.47}$$

where y_i is given. For an ideal mixture where Raoult's law holds this gives

$$\Sigma_i \frac{y_i}{p_i^{\text{sat}}(T)} = \frac{1}{p} \tag{7.48}$$

Example 7.19 Dew point at given temperature T. *A vapor mixture contains 50% pentane (1), 30% hexane (2) and 20% cyclohexane (3) (all in mol-%), i.e.,*

$$y_1 = 0.5; \quad y_2 = 0.3; \quad y_3 = 0.2$$

At $T = 400$ *K, the pressure is gradually increased. What is the dew point pressure and the composition of the first liquid that is formed? Assume ideal liquid mixture and ideal gas (Raoult's law).*

Solution. *The task is to find the value of* p *that satisfies (7.48). Since* T *is given, this is trivial; we can simply calculate* $1/p$ *from (7.48). With the data from Example 7.17 we get:*

$$\frac{1}{p} = \frac{0.5}{10.248} + \frac{0.3}{4.647} = \frac{0.2}{3.358} = 0.1729\text{bar}^{-1}$$

and we find $p = 5.78$ *bar. The liquid phase composition is* $x_i = y_i p / p_i^{\text{sat}}(T)$ *and we find*

$$x_1 = \frac{0.5 \cdot 5.78}{10.248} = 0.282, \quad x_2 = \frac{0.3 \cdot 5.78}{4.647} = 0.373, \quad x_3 = \frac{0.2 \cdot 5.78}{3.749} = 0.345$$

```
% MATLAB:
T=400; y1=0.5; y2=0.3; y3=0.2
psat1=10^(A1-B1/(T+C1)), psat2=10^(A2-B2/(T+C2)), psat3=10^(A3-B3/(T+C3))
p=1/(y1/psat1 + y2/psat2 + y3/psat3)
x1=y1*p/psat1, x2=y2*p/psat2, x3=y3*p/psat3
```

Example 7.20 Dew point at given pressure p. *Consider the same vapor mixture with 50% pentane (1), 30% hexane (2) and 20% cyclohexane (3). At* $p = 5$ *bar, the temperature is gradually decreased. What is the dew point temperature and the composition of the first liquid that is formed?*

Solution. *In this case,* p *and* y_i *are given, and (7.48) provides an implicit equation for* T *which needs to be solved numerically (e.g., using the MATLAB code below). We find* $T = 393.30$ *K, and from* $x_i = y_i p / p_i^{\text{sat}}(T)$ *we find*

$$x_1 = 0.278; \quad x_2 = 0.375; \quad x_3 = 0.347$$

```
% MATLAB:
y1=0.5; y2=0.3; y3=0.2; p=5;
T=fzero(@(T) 1/p-y1/10^(A1-B1/(T+C1))-y2/10^(A2-B2/(T+C2))-y3/10^(A3-B3/(T+C3)) , 400)
```

Example 7.21 Dew point with non-condensable components. *Calculate the temperature and composition of a liquid in equilibrium with a gas mixture containing 10% pentane (1), 10% hexane and 80% nitrogen (3) at 3 bar. Nitrogen is far above its critical point and may be considered non-condensable.*

Solution. *To find the dew-point we use $\Sigma_i x_i = 1$. However, nitrogen is assumed non-condensable so $x_3 = 0$. Thus, this component should not be included in (7.48), which becomes*

$$\frac{y_1}{p_1^{\text{sat}}(T)} + \frac{y_2}{p_2^{\text{sat}}(T)} = \frac{1}{p}$$

Solving this implicit equation in T numerically (e.g., using the MATLAB code below) gives $T = 314.82K$ and from $x_i = y_i p/p_i^{\text{sat}}(T)$ the liquid composition is

$$x_1 = 0.245; \quad x_2 = 0.755; \quad x_3 = 0$$

7.5.3 Flash with liquid and vapor products

Next, consider a **flash** where a feed F (with composition z_i) is split into a vapor product V (with composition y_i) and a liquid product (with composition x_i); see Figure 7.4 on page 189. For each of the N_c components, we can write a material balance

$$Fz_i = Lx_i + Vy_i \tag{7.49}$$

In addition, the vapor and liquid is assumed to be in equilibrium,

$$y_i = K_i x_i$$

The K-values $K_i = K_i(T, P, x_i, y_i)$ are computed from the VLE model. In addition, we have the two relationships $\Sigma_i x_i = 1$ and $\Sigma_i y_i = 1$. With a given feed (F, z_i), we then have $3N_c + 2$ equations in $3N_c + 4$ unknowns $(x_i, y_i, K_i, L, V, T, p)$. Thus, we need two additional specifications, and with these the equation set should be solvable.

pT-flash

The simplest flash is usually to specify p and T (pT-flash), because K_i depends mainly on p and T. Let us show one common approach for solving the resulting equations, which has good numerical properties. Substituting $y_i = K_i x_i$ into the mass balance (7.49) gives $Fz_i = Lx_i + VK_i x_i$, and solving with respect to x_i gives $x_i = (Fz_i/(L + VK_i)$. Here, introduce $L = F - L$ (total mass balance) to derive

$$x_i = \frac{z_i}{1 + \frac{V}{F}(K_i - 1)}$$

Here, we cannot directly calculate x_i because the vapor split V/F is not known. To find V/F we may use the relationship $\Sigma_i x_i = 1$ or alternatively $\Sigma_i y_i = \Sigma_i K_i x_i = 1$. However, it has been found that the combination $\Sigma_i(y_i - x_i) = 0$ results in an equation with good numerical properties; this is the so-called **Rachford-Rice** flash equation[5]

$$\Sigma_i \frac{z_i(K_i - 1)}{1 + \frac{V}{F}(K_i - 1)} = 0 \tag{7.50}$$

which is a monotonic function in V/F and is thus easy to solve numerically. A physical solution must satisfy $0 \leq V/F \leq 1$. If we assume that Raoult's holds, then K_i depends

[5] Rachford, H.H. and Rice, J.D.: "Procedure for Use of Electrical Digital Computers in Calculating Flash Vaporization Hydrocarbon Equilibrium," *Journal of Petroleum Technology*, Sec. 1, p. 19, Oct. 1952.

on p and T only: $K_i = p_i^{\text{sat}}(T)/p$. Then, with T and p specified, we know K_i and the Rachford-Rice equation (7.50) can be solved for V/F. For non-ideal cases, K_i depends also on x_i and y_i, so one approach is add an outer iteration loop on K_i.

Example 7.22 ***pT*-flash.** *A feed F is split into a vapor product V and a liquid product L in a flash tank (see Figure 7.4 on page 189). The feed is 50% pentane, 30% hexane and 20% cyclohexane (all in mol-%). In the tank, $T = 390K$ and $p = 5$ bar. For example, we may have a heat exchanger that keeps constant temperature and a valve on the vapor product stream that keeps constant pressure. We want to find the product split and product compositions. Assume ideal liquid mixture and ideal gas (Raoult's law).*

Comment. *This is a quite close-boiling mixture and we have already found that at 5 bar the bubble point temperature is 382.64 K (Example 7.18) and the dew point temperature is 393.30 K (Example 7.20). The temperature in the flash tank must be between these temperatures for a two-phase solution to exist (which it does in our case since $T = 390$ K).*

Solution. *The feed mixture of pentane (1), hexane (2) and cyclohexane (3) is*

$$z_1 = 0.5; \quad z_2 = 0.3; \quad z_3 = 0.2$$

We have $K_i = p_i^{\text{sat}}(T)/p$ and at $T = 390K$ and p= 5 bar, we find with the Antoine parameters in Table 7.2:

$$K_1 = 1.685, \quad K_2 = 0.742, \quad K_3 = 0.532$$

Now, z_i and K_i are known, and the Rachford-Rice equation (7.50) is solved numerically to find the vapor split $V/F = 0.6915$. The resulting liquid and vapor compositions are (for details see the MATLAB code below):

$$x_1 = 0.3393, \quad x_2 = 0.3651, \quad x_3 = 0.2956$$

$$y_1 = 0.5717, \quad y_2 = 0.2709, \quad y_3 = 0.1574$$

```
% MATLAB:
z1=0.5; z2=0.3; z3=0.2; p=5; T=390;
psat1=10^(A1-B1/(T+C1)); psat2=10^(A2-B2/(T+C2)); psat3=10^(A3-B3/(T+C3));
K1=psat1/p; K2=psat2/p; K3=psat3/p; k1=1/(K1-1); k2=1/(K2-1); k3=1/(K3-1);
% Solve Rachford-Rice equation numerically to find a=V/F:
a=fzero(@(a) z1/(k1+a) + z2/(k2+a) + z3/(k3+a) , 0.5)
x1=z1/(1+a*(K1-1)), x2=z2/(1+a*(K2-1)), x3=z3/(1+a*(K3-1))
y1=K1*x1, y2=K2*x2, y3=K3*x3
```

Example 7.23 Condenser and flash drum for ammonia synthesis. *The exit gas from an ammonia reactor is at 250 bar and contains 61.5% H_2, 20.5% N_2 and 18% NH_3. The gas is cooled to $25^o C$ (partly condensed), and is then separated in a flash drum into a recycled vapor stream V and a liquid product L containing most of the ammonia. We want to calculate the product compositions (L and V) from the flash drum.*

Data. *In spite of the high pressure, we assume for simplicity ideal gas. Use vapor pressure data for ammonia from Table 7.2 and Henry's law coefficients for N_2 and H_2 from page 187. For ammonia, we assume ideal liquid mixture, i.e., $\gamma_{NH3} = 1$ (which is reasonable since the liquid phase is almost pure ammonia).*

Solution. *The feed mixture of H_2 (1), N_2 (2) and NH_3 (3) is*

$$z_1 = 0.615, \quad z_2 = 0.205, \quad z_3 = 0.18$$

For ammonia, we have at $T = 298.15$ K and $p = 250$ bar (Raoult's law):

$$K_3 = \frac{p_3^{\text{sat}}(T)}{p} = \frac{9.83 \text{ bar}}{250 \text{ bar}} = 0.0393$$

For H_2 and N_2, we have from the given data for Henry's coefficient at $25^o C$ (298.15 K):

$$K_1 = \frac{H_1(T)}{p} = \frac{15200 \text{ bar}}{250 \text{ bar}} = 60.8$$

$$K_2 = \frac{H_2(T)}{p} = \frac{8900 \text{ bar}}{250 \text{ bar}} = 35.6$$

Now, z_i and K_i are known, and the Rachford-Rice equation (7.50) is solved numerically to find the vapor split $V/F = 0.8500$. The resulting liquid and vapor compositions of the products are

$$x_1 = 0.0119, \quad x_2 = 0.0067, \quad x_3 = 0.9814$$
$$y_1 = 0.7214, \quad y_2 = 0.2400, \quad y_3 = 0.0386$$

This agrees well with flow sheet data from a commercial ammonia plant.

Other flashes

For other flashes, like the pH**-flash** (which is relevant for an adiabatic flash tank), one must include also the energy balance. For example, for an adiabatic flash tank, the steady-state energy balance gives that the enthalpy H is constant. That is, $H_{\text{in}} = H_{\text{out}}$, and we get

$$\underbrace{Fh_F}_{H} = Vh_V + Lh_L \tag{7.51}$$

where h_V and h_L [kJ/mol; kJ/kg] depend primarily on T, but in general also on x_i, y_i and p. One solution approach is to use the pT-flash described above, and iterate on T in an outer loop until the requirement on H is satisfied. Another approach is to solve the equations simultaneously, as shown for the dynamic adiabatic flash of methanol and ethanol in Example 11.18 (page 317).

7.5.4 Flash exercises

Exercise 7.8* Bubble and dew point at given temperature. *A hydrocarbon mixture contains 10% propane, 80% hexane and 10% dodecane. (a) Find the bubble point pressure at 300 K. (b) Find the dew point pressure at 300 K.*

Exercise 7.9* Bubble and dew point at given pressure. *A hydrocarbon mixture contains 10 mol-% propane, 80% hexane and 10% dodecane. (a) Find the bubble point temperature at 1 bar. (b) Find the dew point temperature at 1 bar.*

Exercise 7.10 Bubble point at given pressure. *A liquid mixture contains 4 mol-% hexane and the rest is octane. What is the composition of the first vapor formed if the total pressure is 1 atm?*

Exercise 7.11* Flash at given p and T. *A feed to a flash tank is 100 mol/s and contains 10% propane, 80% hexane and 10% dodecane. Find the amount of vapor product and the compositions when $T = 350K$ and $p = 2bar$.*

Exercise 7.12 Flash calculation for binary mixture. *Calculate the amount of liquid that will remain at equilibrium when a mixture of 7 kg hexane and 3 kg toluene is vaporized at $95^o C$ and 1.5 bar.*

Data: Molecular weights are 86.17 and 92.13.

Exercise 7.13 * Bubble and dew point calculations. *(a) A gas mixture of 15 mol-% benzene, 5 mol-% toluene and the rest nitrogen is compressed isothermally at 100°C until condensation occurs. What will be the composition of the initial condensate?*

(b) Calculate the temperature and composition of a vapor in equilibrium with a liquid that is 25 mol-% benzene and 75 mol-% toluene at 1 atm. Is this a bubble point or a dew point?

(c) Calculate the temperature and composition of a liquid in equilibrium with a gas mixture containing 15 mol-% benzene, 25 mol-% toluene and the rest nitrogen (which may be considered non-condensable) at 1 atm. Is this a bubble point or a dew point?

Exercise 7.14 Condenser for exhaust gas. *The exhaust gas from a natural gas power plant is at 1 bar and contains 76% N_2 (1), 12% O_2 (2), 4% CO_2 (3) and 8% H_2O (4). The gas is cooled to $25^o C$ (partly condensed), and is then separated in a flash drum into a gas product V and a liquid product L containing most of the water. Find the compositions of the product streams. Are we able to remove any significant amount of CO_2 in the water?*

Data: Use pure component vapor pressure data for water and Henry's law coefficients for the gas components (see page 187).