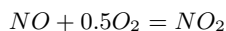


```
% H, S, G and K for reaction N2 + 3 H2 = 2 NH3
dhrT = 2*hfT_nh3 - hfT_n2 - 3*hfT_h2
dsrT = 2*sfT_nh3 - sfT_n2 - 3*sfT_h2
dgrT = dhrT - T*dsrT
K = exp(-dgrT/(8.3145*T))
```

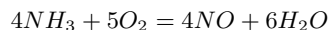
Extracted from the book:
 S. Skogestad, "Chemical and Energy Process Engineering",
 CRC Press (Taylor and Francis), 2009.

Exercise 7.3* NO_x equilibrium. A gas mixture at $940^\circ C$ and 2.5 bar consists of 5% O_2 , 11% NO , 16% H_2O and the rest N_2 . The formation of NO_2 is neglected, and you need to check whether this is reasonable by calculating the ratio (maximum) between NO_2 and NO that one would get if the reaction



was in equilibrium at $940^\circ C$. **Data.** Assume constant heat capacity and use data for ideal gas from page 416.

Exercise 7.4 Consider the gas phase reaction



(a) Calculate standard enthalpy, entropy, Gibbs energy and the equilibrium constant for the reaction at 298 K and 1200 K.

(b) Calculate the equilibrium composition at 1200 K and 8 bar when the feed consists of 10 mol-% ammonia, 18 mol-% oxygen and 72 mol-% nitrogen.

(c) What is the feed temperature if the reactor operates adiabatically?

Data. Assume constant heat capacity and use data for ideal gas from page 416.

7.4 Introduction to vapor/liquid equilibrium

Phase equilibrium, and in particular vapor/liquid-equilibrium (VLE), is important for many process engineering applications. The thermodynamic basis for phase equilibrium is the same as for chemical equilibrium, namely that the Gibbs energy G is minimized at a given T and p (see page 174).

7.4.1 General VLE condition for mixtures

Vapor/liquid-equilibrium (VLE) for mixtures is a large subject, and we will here state the general equilibrium condition, and then give some applications. The fact that the Gibbs energy G is minimized at a given temperature T and pressure p implies that a necessary equilibrium condition is that G must remain constant for any small perturbation, or mathematically $(dG)_{T,p} = 0$ (see page 385). Consider a small perturbation to the equilibrium state where a small amount dn_i of component i evaporates from the liquid phase (l) to the vapor/gas phase (g). The necessary equilibrium condition at a given T and p then gives

$$dG = (\bar{G}_{g,i} - \bar{G}_{l,i})dn_i = 0 \quad (7.26)$$

where \bar{G}_i [J/mol i] is the partial Gibbs energy, also known as the **chemical potential**, $\mu_i \triangleq \bar{G}_i$. Since (7.26) must hold for any value of dn_i , we derive the equilibrium

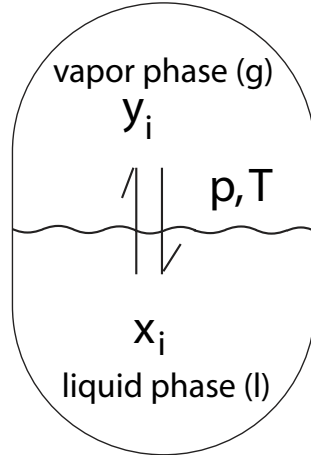


Figure 7.3: Vapor/liquid equilibrium (VLE)

condition $\bar{G}_{g,i} = \bar{G}_{l,i}$. That is, the VLE-condition is that the chemical potential for any component i is the same in both phases,

$$\mu_{g,i} = \mu_{l,i} \quad (7.27)$$

7.4.2 Vapor pressure of pure component

Let us first consider VLE for a pure component. The component vapor pressure $p^{\text{sat}}(T)$ is the equilibrium (or **saturation**) pressure for the pure liquid at temperature T . As the temperature increases, the molecules in the liquid phase move faster and it becomes more likely that they achieve enough energy to escape into the vapor phase, so the vapor pressure increases with temperature. For example, the vapor pressure for water is 0.0061 bar at 0 °C, 0.03169 bar at 25 °C, 1.013 bar at 100 °C, 15.54 bar at 200 °C and $p_c = 220.9$ bar at $T_c = 374.1$ °C (critical point).

As the temperature and resulting vapor pressure increases, the molecules come closer together in the gas phase, and eventually we reach the **critical point** (at temperature T_c and pressure p_c), where there is *no difference between the liquid and gas phases*. For a pure component, the **critical temperature** T_c is the highest temperature where a gas can condense to a liquid, and the vapor pressure is therefore only defined up to T_c . The corresponding **critical pressure** p_c is typically around 50 bar, but it can vary a lot, e.g., from 2.3 bar (helium) to 1500 bar (mercury).

For a pure component, the *exact Clapeyron equation* provides a relationship between vapor pressure and temperature,

$$\frac{dp^{\text{sat}}}{dT} = \frac{\Delta_{\text{vap}}S}{\Delta_{\text{vap}}V} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} \quad (7.28)$$

Here $\Delta_{\text{vap}}H = H_g - H_l$ [J/mole] is the heat of vaporization at temperature T and

$\Delta_{\text{vap}}V = V_g - V_l$ [m^3/mol] is the difference in molar volume between the phases. An equivalent expression applies for the vapor pressure over a pure solid.

Derivation of (7.28): From (7.27) the necessary equilibrium condition is $G_g = G_l$. Assume that there is a small change in T which results in a small change in p . From (B.66), the resulting changes in Gibbs energy are $dG_l = V_l dp - S_l dT$ and $dG_g = V_g dp - S_g dT$. Since the system is still in equilibrium after the change, we must have $dG_l = dG_g$ which gives $(V_g - V_l)dp - (S_g - S_l)dT$. The Clapeyron equation follows by noting that $\Delta_{\text{vap}}S = \Delta_{\text{vap}}H/T$, see (7.8).

In most cases, we have $V_g \gg V_l$, and for ideal gas we have $V_g = p/RT$ and from (7.28) we then derive, by using $\frac{1}{p}dp = d \ln p$, the *approximate Clausius-Clapeyron equation*,

$$\frac{d \ln p^{\text{sat}}(T)}{dT} = \frac{\Delta_{\text{vap}}H(T)}{RT^2} \quad (7.29)$$

which applies for a pure component at low pressure, typically less than 10 bar. If the heat of vaporization $\Delta_{\text{vap}}H$ is constant (independent of T ; which indeed is somewhat unrealistic since it decreases with temperature and is 0 in the critical point), we derive from (7.29) the *integrated Clausius-Clapeyron equation*,

$$p^{\text{sat}}(T) = p^{\text{sat}}(T_0) \exp \left[-\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (7.30)$$

which is sometimes used to compute the vapor pressure at temperature T given $p^{\text{sat}}(T_0)$ at temperature T_0 . However, (7.30) is not sufficiently accurate for practical calculations, so instead empirical relationships are used. A popular one is the **Antoine equation**,²

$$\ln p^{\text{sat}}(T) = A - \frac{B}{T + C} \quad (7.31)$$

Note that (7.30) is in the form (7.31) with $A = \ln p^{\text{sat}}(T_0) + \Delta_{\text{vap}}H/RT_0$, $B = \Delta_{\text{vap}}H/R$ and $C = 0$. Antoine parameters for some selected components are given in Table 7.2 (page 190).

Example 7.13 For water, we find in an older reference book the following Antoine constants: $A = 18.3036$, $B = 3816.44$ and $C = -46.13$. This is with pressure in [mm Hg] and temperature in [K] (note that these Antoine parameters are different from those given in Table 7.2). The vapor pressure at 100 °C is then

$$p^{\text{sat}}(373.15 \text{ K}) = e^{18.3036 - \frac{3816.44}{(373.15 - 46.13)}} = 759.94 \text{ mmHg} = \frac{759.94}{750.1} \text{ bar} = 1.013 \text{ bar}$$

which agrees with the fact that the boiling temperature for water is 100 °C at 1 atm = 1.01325 bar.

Engineering rule for vapor pressure of water. The following simple formula, which is easy to remember, gives surprisingly good estimates of the vapor pressure for water for temperatures from 100°C (the normal boiling point) and up to 374°C (the critical point):

$$p_{\text{H}_2\text{O}}^{\text{sat}}[\text{bar}] = \left(\frac{t[^\circ\text{C}]}{100} \right)^4 \quad (7.32)$$

² Numerical values for the three Antoine constants A , B and C are found in many reference books (for example, B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The properties of gases and liquids*, 5th Edition, McGraw-Hill, 2001.

This formula is very handy for engineers dealing with steam at various pressure levels. For example, from the formula we estimate $p^{\text{sat}} \approx 1$ bar at 100°C (the correct value is $1 \text{ atm} = 1.013 \text{ bar}$) and $p^{\text{sat}} \approx 2^4 = 16$ bar at 200°C (the correct value is 15.53 bar).

Exercise 7.5* Test the validity of the simple formula (7.32), by comparing it with the following experimental vapor pressure data for water:

$t[^\circ\text{C}]$	0	25	50	75	100	120	150	200	250	300	$374.14(t_c)$
$p[\text{bar}]$	0.00611	0.03169	0.1235	0.3858	1.013	1.985	4.758	15.53	39.73	85.81	$220.9(p_c)$

Also test the validity of the two alternative sets of Antoine constants for water (given in Example 7.13 and Table 7.2).

Exercise 7.6* **Effect of barometric pressure on boiling point.** Assume that the barometric (air) pressure may vary between 960 mbar (low pressure) and 1050 mbar (high pressure). What is the corresponding variation in boiling point for water?

Comment. Note the similarity between Clausius-Clapeyron's equation (7.29) for the temperature dependency of vapor pressure,

$$\frac{d \ln p^{\text{sat}}(T)}{dT} = \frac{\Delta_{\text{vap}}H(T)}{RT^2}$$

and van't Hoff's equation (7.25) for the temperature dependency of the chemical equilibrium constant K ,

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus(T)}{RT^2}$$

This is of course not a coincidence, because we can view evaporation as a special case of an endothermic "chemical reaction."

7.4.3 VLE for ideal mixtures: Raoult's law

Here, we consider vapor/liquid equilibrium of mixtures; see Figure 7.3 (page 180). Let

x_i - mole fraction of component i in the liquid phase

y_i - mole fraction of component i in the vapor phase

The simplest case is an *ideal liquid mixture* and *ideal gas* where **Raoult's law** states that for any component i , the partial pressure $p_i = y_i p$ equals the vapor pressure of the pure component i multiplied by its mole fraction x_i in the liquid phase, that is,

$$\text{Raoult's law : } y_i p = x_i p_i^{\text{sat}}(T) \quad (7.33)$$

A simple molecular interpretation of Raoult's law is that in an ideal liquid mixture the fraction of i -molecules at the surface is x_i , so the partial pressure $p_i = y_i p$ is reduced from $p_i^{\text{sat}}(T)$ (pure component) to $x_i p_i^{\text{sat}}(T)$ (ideal mixture).

Thermodynamic derivation of Raoult's law. A thermodynamic derivation is useful because it may later be generalized to the non-ideal case. We start from the general VLE condition $\mu_{g,i} = \mu_{l,i}$ in (7.27), which says that the chemical potential (= partial Gibbs energy) for each component is the same in both phases at the given p and T . Now, Gibbs energy is a state function, and we can also imagine another route for taking component i from the liquid to the vapor phase, consisting of four steps (all at temperature T): (1) Take component i out of the liquid mixture. From (B.41) the change in chemical potential for this "unmixing" is $\Delta\mu_{i,1} = -RT \ln a_i$ where the activity is $a_i = \gamma_i x_i$. For an **ideal liquid mixture** the activity coefficient is 1, $\gamma_i = 1$. (2) Take the pure component as

liquid from pressure p to the saturation pressure $p_i^{\text{sat}}(T)$. Since the liquid volume is small this gives a very small change in chemical potential, known as the **Poynting factor**, which we here neglect, i.e., $\Delta\mu_{i,2} \approx 0$. (3) Evaporate the pure component at T and $p_i^{\text{sat}}(T)$. Since we have equilibrium ($\Delta G = 0$) there is no change in the chemical potential, $\Delta\mu_{i,3} = 0$. (4) In the gas phase, go from pure component at pressure $p_i^{\text{sat}}(T)$ to a mixture at p where the partial pressure is p_i . From (B.40), the change in chemical potential for an **ideal gas** is $\Delta\mu_{i,4} = RT \ln(p_i/p_i^{\text{sat}}(T))$. Now, since the initial and final states are in equilibrium, the sum of the change in chemical potential for these four steps should be zero and we derive $-RT \ln x_i + RT \ln(p_i/p_i^{\text{sat}}(T)) = 0$ and Raoult's law follows.

7.4.4 Relative volatility

The relative volatility α is a very useful quantity. For example, it is used for short-cut calculations for distillation columns.³ For a mixture, the **relative volatility** α between the two components L (the “light” component) and H (the “heavy” component) is defined as

$$\alpha \triangleq \frac{y_L/x_L}{y_H/x_H} \quad (7.34)$$

For an **ideal mixture** where Raoult's law (7.33) applies, we then have

$$\alpha = \frac{y_L/x_L}{y_H/x_H} = \frac{p_L^{\text{sat}}(T)}{p_H^{\text{sat}}(T)} \quad (7.35)$$

that is, α equals the ratio between the pure component's vapor pressures. Furthermore, we see from (7.30) that if the heat of vaporization for the two components are similar, then α does not change much with the temperature.

The approximation of **constant relative volatility** (independent of composition and temperature) is often used in practical calculations, and is based on the following assumptions

- Ideal liquid mixture such that Raoult's law applies (α is then independent of composition)
- The components have similar heat of vaporization (α is then independent of temperature)

These assumptions generally hold well for separation of “similar” components. However, the assumption of constant α is poor for many non-ideal mixtures. For example, for a mixture that forms an azeotrope, like water and ethanol, we have $\alpha = 1$ at the azeotropic point, with $\alpha > 1$ on one side and $\alpha < 1$ on the other side of the azeotrope (that is, even the order of “heavy” (H) and “light” (L) depends on the liquid composition).

Relative volatility from boiling point data. For ideal mixtures that follow Raoult's law, the following approximate relationship between the relative volatility α and the boiling point difference $T_{bH} - T_{bL}$ for the components applies:

$$\alpha \approx \exp \left[\frac{\Delta_{\text{vap}}H}{RT_b} \cdot \frac{T_{bH} - T_{bL}}{T_b} \right] \quad (7.36)$$

³ For more on distillation see, for example, I.J. Halvorsen, S. Skogestad: “Distillation Theory,” *Encyclopedia of Separation Science*, D. Wilson (Editor-in-chief), Academic Press, 2000 (available at S. Skogestad's homepage).

Here $T_b = \sqrt{T_{bH} \cdot T_{bL}}$ is the geometric mean boiling point, and $\Delta_{\text{vap}}H$ is the average heat of vaporization for the two components at the average boiling point T_b . From Trouton's rule (see page 378), a typical value is $\frac{\Delta_{\text{vap}}H}{RT_b} \approx \frac{85\text{J/mol K}}{8.31\text{J/mol K}} = 10.2$.

Derivation of (7.36). We assume that Raoult's law holds such that (7.35) holds. If we assume that the heat of vaporization is independent of temperature, then the integrated Clausius-Clapeyron equation (7.30) gives for component L if we choose $T = T_{bH}$ and $T_0 = T_{bL}$:

$$p_L^{\text{sat}}(T_{bH}) = p_L^{\text{sat}}(T_{bL}) \exp \left[-\frac{\Delta_{\text{vap}}H_L}{R} \left(\frac{1}{T_{bH}} - \frac{1}{T_{bL}} \right) \right]$$

In practice, $\Delta_{\text{vap}}H_L$ depends on temperature, so an average value for the temperature interval from T_{bL} to T_{bH} should be used. At the normal boiling points, $p_L^{\text{sat}}(T_{bL}) = p_H^{\text{sat}}(T_{bH}) = 1 \text{ atm}$, and the relative volatility at $T = T_{bH}$ becomes

$$\alpha = \frac{p_L^{\text{sat}}(T_{bH})}{p_H^{\text{sat}}(T_{bH})} = \exp \left[-\frac{\Delta_{\text{vap}}H_L}{R} \left(\frac{1}{T_{bH}} - \frac{1}{T_{bL}} \right) \right]$$

A similar expression for α at $T = T_{bL}$ is derived by considering component H , and combining the two yields (7.36). \square

Example 7.14 Let us use (7.36) to calculate an approximate value for relative volatility for the mixture methanol (L) - ethanol (H). We obtain the following data for the pure components

$$\text{Methanol : } T_{bL} = 337.8\text{K}; \Delta_{\text{vap}}H_L(T_{bL}) = 35.2 \text{ kJ/mol}$$

$$\text{Ethanol : } T_{bH} = 351.5\text{K}; \Delta_{\text{vap}}H_B(T_{bH}) = 40.7 \text{ kJ/mol}$$

The geometric mean boiling point is $T_b = 344.6 \text{ K}$, the average heat of vaporization is $\Delta_{\text{vap}}H = (\Delta_{\text{vap}}H_L(T_{bL}) + \Delta_{\text{vap}}H_B(T_{bH}))/2 = 37.9 \text{ kJ/mol}$ and we get $\Delta_{\text{vap}}H/RT_b = 13.25$ (which is higher than the value of 10.2 according to Trouton's rule). The boiling point difference is 13.7 K, and assuming ideal mixture, (7.36) gives $\alpha \approx \exp \frac{12.90 \cdot 13.7}{344.6} = 1.69$. The experimental value is about 1.73.

We emphasize that the simplified formula (7.36) is primarily intended to provide insight, and one should normally obtain experimental data for the vapor/liquid equilibrium or use a more exact model.⁴

7.4.5 Boiling point elevation and freezing point depression

Consider a mixture consisting mainly of a volatile component (the solvent A) with some dissolved non-volatile component (the solute B). For example, this could be a mixture of water (A) and sugar (B). Such a solution has a higher boiling point than the pure component (e.g., water), and we want to find the boiling point elevation ΔT_b . For a *dilute* ideal mixture (solution) with mole fraction x_B of the non-volatile component, we derive that the **boiling point elevation** is

$$\Delta T_b = T_b - T_b^* = \frac{RT_b^{*2} x_B}{\Delta_{\text{vap}}H} \quad (7.37)$$

where T_b^* is the boiling point of the pure component A, and T_b is the boiling point of the mixture. If the solution is *not dilute* then x_B should be replaced by $\ln \frac{1}{1-x_B}$.

⁴ A comprehensive reference work for experimental vapor/liquid equilibrium data for mixtures is: J. Gmehling and U. Onken, *Vapor-liquid equilibrium data collection*, Dechema Chemistry Data Series (1977-).

Proof of (7.37). For an ideal mixture (solution), Raoult's law (7.33) gives that the partial pressure of the solvent (A) is $p_A = (1 - x_B)p_A^{\text{sat}}(T)$ where p_A is equal to the total pressure p since the other component is non-volatile. At the boiling point of the mixture, the total pressure is $p_0 = 1$ atm and we get $p_0 = (1 - x_B)p_A^{\text{sat}}(T_b)$. Here, from the integrated Clausius-Clapeyron equation (7.30) we have for the solvent $p_A^{\text{sat}}(T_b) = p_A^{\text{sat}}(T_b^*) \exp\left[-\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_b} - \frac{1}{T_b^*}\right)\right]$. Here, $p_A^{\text{sat}}(T_b^*) = p_0 = 1$ atm (since the vapor pressure of a pure component is 1 atm at the normal boiling point), and by combining and taking the log on both sides we derive

$$\ln \frac{1}{1 - x_B} = \frac{\Delta_{\text{vap}}H}{R} \frac{T_b - T_b^*}{T_b^* T_b}$$

(7.37) follows by assuming a dilute solution ($x_B \rightarrow 0$) where $\ln \frac{1}{1 - x_B} \approx x_B$ and $T_b^* \approx T_b$. An alternative derivation is to start from the general equilibrium condition $\mu_{g,A} = \mu_{l,A}$ in (7.27). Here $\mu_{l,A} = \mu_{l,a}^* + RT \ln x_A$ for an ideal mixture and $\mu_{g,A} = \mu_{g,A}^*$ because B is non-volatile. Using $\mu_{g,A}^* - \mu_{l,a}^* = \Delta_{\text{vap}}G$, etc. leads to the desired results; for details see a physical chemistry textbook.

The reason for the boiling point elevation is that the dissolved components (B) make it more favorable from an entropy point of view for the solvent to remain the liquid phase. The same argument (that the solvent likes to remain in the liquid phase) also applies for freezing, and it can be proved that for a dilute ideal mixture the **freezing (melting) point depression** is

$$\Delta T_m = T_m^* - T_m = \frac{RT_m^{*2} x_B}{\Delta_{\text{fus}}H} \quad (7.38)$$

where T_m^* is the melting (freezing) point of the pure component, T_m the melting point of the mixture and $\Delta_{\text{fus}}H$ is the heat of melting.

In both (7.37) and (7.38), x_B is the sum of the mole fractions of all dissolved components (non-volatile or non-freezing). If a component dissociates (e.g., into ions), then this must be taken into account (see the sea water example below).

Remark. Note that both the boiling point elevation (7.37) and the freezing point depression (7.38) depend only on the concentration (mole fraction x_B) of the dissolved component (solute), and not on what component we have. Another such property is the osmotic pressure over an ideal membrane (see page 382). These three properties are referred to as **colligative solution properties**. They can, for example, be used to determine the molar mass (M) of a molecule (see Exercise 7.7).

Example 7.15 Boiling point elevation and freezing point depression of seawater.

We first need to find the mole fraction x_B of dissolved components. We assume that the salinity of seawater is 3.3%, that is, 1 l seawater contains 33 g/l of salt (NaCl). Since the molar mass of NaCl is 58.4 g/mol, we have that 33 g/l corresponds to $(33 \text{ g/l}) / (58.4 \text{ g/mol}) = 0.565 \text{ mol/l}$ of NaCl. However, when dissolved in water, NaCl splits in two **ions**, Na^+ and Cl^- . Now, 1 l of water is 55.5 mol ($= (1000 \text{ g}) / (18 \text{ g/mol})$). Thus, 1 l of seawater consists of approximately 0.565 mol/l Na^+ , 0.565 mol/l Cl^- and 55.5 mol water, and the corresponding mole fractions are approximately 0.01 (Na^+), 0.01 (Cl^-) and 0.98 (H_2O). The total mole fraction of dissolved components in seawater is then $x_B = x_{\text{Na}} + x_{\text{Cl}} = 0.01 + 0.01 = 0.02$.

Water has a boiling point of $T_b^* = 373.15 \text{ K}$ (100 °C) and the heat of vaporization at the boiling point is $\Delta_{\text{vap}}H = 40.66 \text{ kJ/mol}$. Thus, from (7.37) the boiling point elevation is

$$\Delta T_b = T_b - T_b^* = \frac{8.31 \cdot 373.15^2 \cdot 0.02}{40666} \text{ K} = 0.57 \text{ K}$$

so the **boiling point of seawater** is about 100.57 °C.

Water has a freezing (melting) point of $T_m^* = 273.15 \text{ K}$ (0°C) and the heat of fusion (melting) at the freezing point is $\Delta_{\text{fus}}H = 6.01 \text{ kJ/mol}$. Thus, from (7.38) the freezing point depression is

$$\Delta T_m = T_m^* - T_m = \frac{8.31 \cdot 273.15^2 \cdot 0.02}{6010} \text{ K} = 2.06 \text{ K}$$

so the freezing point of seawater is about -2.06°C .

Exercise 7.7 Adding 7 g of an unknown solute to 100 g water gives a boiling point elevation of 0.34°C . Estimate the molar mass of the unknown solute, and the corresponding freezing point depression.

7.4.6 VLE for dilute mixtures: Henry's law

Raoult's law cannot be used for "supercritical" components ("gases"), where T is above the critical temperature T_c for the component. This is because $p^{\text{sat}}(T)$ is only defined for $T \leq T_c$. However, also supercritical components have a solubility in liquids. For example CO_2 can be dissolved in water at 50°C even though the critical temperature for CO_2 is 31°C . "Fortunately," the concentration in the liquid phase of supercritical (and other "light") components is usually low. For sufficiently dilute mixtures (low concentrations), there is a generally linear relationship between a component's gas phase fugacity ("thermodynamic partial pressure") and its liquid concentration, even for non-ideal mixtures. This gives Henry's law, which also applies to supercritical components,

$$\text{Henry's law : } f_i^V = H_i(T) \cdot x_i \quad (x_i \rightarrow 0) \quad (7.39)$$

Here, Henry's constant H_i [bar] is a function of temperature only (at least at pressure below 50 bar; at very high pressures we need to include the "Poynting factor" for the pressure's influence on the liquid phase). If the pressure p is sufficiently low, we can assume ideal gas phase where $f_i^V = p_i = y_i p$ (the partial pressure), and Henry's law (7.39) becomes

$$y_i = \frac{H_i}{p} x_i \quad (x_i \rightarrow 0, \text{ low } p) \quad (7.40)$$

Henry's law on the form (7.40) is valid for dilute solutions ($x_i < 0.03$, typically) and low pressures ($p < 20$ bar, typically). For an ideal mixture (liquid phase), Henry's constant H_i equals the component's vapor pressure (compare (7.33) and (7.40)), and Henry's constant is therefore expected to increase with temperature. Thus, the solubility is expected to be lower at high temperature. However, there are exceptions to this rule, as seen below for the solubility of H_2 and N_2 in ammonia.

Water. Henry's constant for the solubility of some gases in water at 0°C and 25°C is given in Table 7.1. Note from the critical data on page 416 that most of these gases are supercritical at these temperatures. Thus, they cannot form a pure liquid phase, but they can dissolve in liquid water. In all cases, Henry's constant increases with temperature. For example, for the solubility of CO_2 in water, Henry's constant increases from 740 bar at 0°C , to 1670 bar at 25°C and to 3520 bar at 60°C .

Ammonia. The following values for Henry's constant for the solubility of H_2 and N_2 in ammonia were obtained using the SRK equation of state with interaction parameters $k_{ij} = 0.226$ between ammonia and nitrogen and $k_{ij} = 0$ between ammonia

Table 7.1: Henry's constant for the solubility of some gases in water

component	H_i [bar]	H_i [bar]
i	(0°C)	(25°C)
H_2	58200	71400
N_2	53600	84400
CO	35700	60000
O_2	25800	44800
CH_4	22700	41500
C_2H_4	5570	11700
CO_2	740	1670
Cl_2	–	635
H_2S	270	545

and hydrogen:

Component	H_i [bar]	H_i [bar]
i	(-25°C)	(25°C)
H_2	48000	15200
N_2	26000	8900

We note that H_i for both components *decrease* by a factor of about 3 as the temperature is increased from -25°C to 25°C . We then have the unexpected result that the solubility of these gases in ammonia is higher at high temperature.

Example 7.16 The partial pressure of CO_2 over a water solution at 25°C is 3 bar. Task: (a) Calculate the concentration of CO_2 in the solution [mol/l]. (b) Find the volume of $CO_2(g)$ at 1 atm and 25°C that is dissolved in 1 l solution.

Solution. (a) We assume ideal gas and dilute solution. From Henry's law, we have that $p_i = H_i x_i$, where $H_i = 1670$ bar (Table 7.1) and $p_i = 3$ bar. This gives $x_i = 3/1670 = 0.0018$ [mol CO_2 /mol] (which confirms that we have a dilute solution). In 1 l of solution the amount of water is (1 kg)/($18 \cdot 10^{-3}$ kg/mol) = 55.5 mol. That is, the concentration of CO_2 is $c_i = x_i \cdot 55.5$ mol/l = 0.10 mol/l.

(b) The molar volume of an ideal gas at 1 atm and 25°C is $V_m = RT/p = 8.31 \cdot 298.15/1.01325 \cdot 10^5 = 0.02445$ $m^3/mol = 24.45$ l/mol. In 1 l solution, there is 0.10 mol CO_2 , and the corresponding volume of this as gas at 1 atm is then 2.45 l.

7.4.7 VLE for real (non-ideal) mixtures

In this section, we summarize the equations used for calculation of vapor/liquid equilibrium for non-ideal mixtures. It is intended to give an overview, and you need to consult other books for practical calculations. Three fundamentally different methods are

1. Based on K values
2. Based on activity coefficients (for non-ideal mixtures of sub-critical components at moderate pressures)
3. Based on the same equation of state for both phases (for moderately non-ideal mixtures at all pressures)

1. K-value

The K-value is defined for each component as the ratio

$$K_i = \frac{y_i}{x_i} \quad (7.41)$$

where x_i is the mole fraction in the liquid phase and y_i is the mole fraction in the gas phase at equilibrium. Generally, the “K value” is a function of temperature T , pressure p and composition (x_i and y_i). For ideal liquid mixtures and ideal gas, we have from (7.33) that $K_i = p_i^{\text{sat}}(T)/p$, that is, the K value is independent of composition. For dilute mixtures, even non-ideal, we have from Henry’s law (7.40) that $K_i = H_i(T)$. More generally, the K-value can be calculated from one of the two methods given below.

2. Activity coefficient

This method provides a generalization of Raoult’s law to **non-ideal mixtures** and to real gases. From the general VLE-condition $\mu_{g,i} = \mu_{l,i}$ we derive for mixtures of subcritical components: (the proof follows the derivation given for Raoult’s law on page 182)

$$\underbrace{\phi_i^V \cdot y_i \cdot p}_{f_i^V} = \underbrace{\gamma_i \cdot x_i \cdot \phi_i^{\text{sat}} \cdot p_i^{\text{sat}}(T)}_{f_i^L} \cdot \exp \left[\frac{1}{RT} \int_{p_i^{\text{sat}}}^p \bar{V}_i^L dp \right] \quad (7.42)$$

where f_i^V is the fugacity in the vapor phase and f_i^L is the fugacity in the liquid phase. The fugacity coefficients $\phi_i^V(T, p, y_i)$ and $\phi_i^{\text{sat}}(T)$ are 1 for ideal gases, and for real gases their value are usually computed from an equation of state for the gas phase, e.g., SRK. The **activity coefficients** γ_i depend mainly on the liquid composition (x_i) and are usually computed from empirical equations, such as the *Wilson*, NRTL, UNIQUAC and UNIFAC equations, based on experimental interaction data for all binary combinations. The exception is the UNIFAC equation which only requires interaction data for the groups in the molecule. The last exponential term is the so-called Poynting factor for the pressure’s influence on the liquid phase (see the derivation for Raoult’s law on page 182). It is close to 1, except at high pressures above about 50 bar.

At moderate pressures (typically, less than 10 bar) we can assume ideal gas, $\phi_i^V = 1$ and $\phi_i^{\text{sat}} = 1$, and from (7.42) we derive a commonly used relation:

$$\text{Nonideal mixture at moderate pressures : } y_i p = \gamma_i x_i p_i^{\text{sat}} \quad (7.43)$$

For low concentrations of supercritical components we can use Henry’s law, $y_i p = H_i x_i$. For an ideal liquid mixture we have $\gamma_i = 1$ and we rederive from (7.43) Raoult’s law: $y_i p = x_i p_i^{\text{sat}}$.

3. Same equation of state for both phases

For mixtures that do deviate too much from the ideal (for example, for hydrocarbon mixtures), we can use the same reference state (ideal gas) and the same equation

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

$$\phi_i^V y_i = \phi_i^L x_i \quad (7.44)$$

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

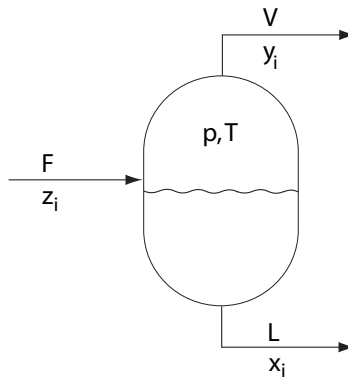


Figure 7.4: Flash tank

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:

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

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 ($V \geq 0$) 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, $\sum y_i = 1$ or

$$\sum_i K_i x_i = 1 \quad (7.45)$$

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

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

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 $T = 400\text{ K}$, 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 $T = 400\text{ K}$. Using the Antoine data in Table 7.2, we get:

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

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

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

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 $p = 5\text{ bar}$, 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 $T = 382.64\text{ K}$, 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 $\sum x_i = 1$ or

$$\sum_i y_i / K_i = 1 \quad (7.47)$$

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

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

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 $\sum_i x_i = 1$. 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 $T = 314.82\text{K}$ 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

$$Fz_i = Lx_i + Vy_i \quad (7.49)$$

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 $\sum_i x_i = 1$ and $\sum_i y_i = 1$. 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 $\sum_i x_i = 1$ or alternatively $\sum_i y_i = \sum_i K_i x_i = 1$. However, it has been found that the combination $\sum_i (y_i - x_i) = 0$ results in an equation with good numerical properties; this is the so-called **Rachford-Rice** flash equation⁵

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

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, $T = 390\text{K}$ 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 $T = 390\text{K}$ 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°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., $\gamma_{\text{NH}_3} = 1$ (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°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

$$\underbrace{Fh_F}_H = Vh_V + Lh_L \quad (7.51)$$

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 $T = 350\text{K}$ and $p = 2\text{bar}$.

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°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% N₂ (1), 12% O₂ (2), 4% CO₂ (3) and 8% H₂O (4). The gas is cooled to 25° 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 CO₂ in the water?

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