Chapter 22
Phase Equilibrium in Mixtures

22.1 Phase Mixtures

In this chapter we discuss equilibria between mixtures in different phases, e.g. liquid-vapor equilibria, or liquid-solid equilibria. Phase mixtures normally are characterized by different mole fractions (or concentrations) in the different phases. We shall discuss phase diagrams, changes of melting and evaporation temperatures in solutions, distillation processes, and gas solubility.

22.2 Gibbs' Phase Rule

In extension to our previous notation we introduce Latin superscripts to denote the phases, and we assume that we have f different phases. For instance X_α^j $(\alpha = 1, \ldots, \nu,\ j = 1, , \ldots, f)$ denotes the mole fraction of component α in phase j. Also, $\mu_\alpha^j \left(T, p, X_\beta^j\right)$ is the chemical potential of component α in phase j; note that the chemical potential depends only on the mole fractions of the same phase.

For each phase, the mole fractions sum to unity, that is

$$\sum_{\beta=1}^{\nu} X_\beta^j = 1 \quad \text{for } j = 1, 2, \ldots, f\ . \tag{22.1}$$

It follows that a mixture with ν components in f phases is characterized by $(\nu - 1) f$ independent mole fractions. In addition, pressure p and temperature T are variables, so that the mixture is characterized by $(\nu - 1) f + 2$ intensive variables, $\left\{p, T, X_\alpha^j\right\}$.

Phase boundaries are permeable interfaces between phases that allow all components to pass, and thus in equilibrium the chemical potentials of all components must be continuous between any two phases,

$$\bar{\mu}_\alpha^1 = \bar{\mu}_\alpha^2 = \cdots = \bar{\mu}_\alpha^f \quad \text{for } \alpha = 1, \ldots, \nu\ . \tag{22.2}$$

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These equations are known as Gibbs' phase rule, and they give $(f-1)\,\nu$ conditions[1] that restrict the $(\nu-1)\,f+2$ variables. The difference between these numbers gives the number of degrees of freedom for the system,

$$\mathrm{F} = [(\nu-1)\,f+2] - [(f-1)\,\nu] = 2+\nu-f\ . \tag{22.3}$$

That is, we can freely chose F properties of the mixture, while the remaining $(f-1)\,\nu$ properties are then fixed through Gibbs' phase rule.

We consider this rule for the simple example of a single component, where $\nu = 1$. The variables are (p, T) and we find $\mathrm{F} = 3 - f$.

In a single phase, we have $f = 1$, so that there are $\mathrm{F} = 2$ degrees of freedom: p and T can be chosen independently.

When there are two phases, either liquid-vapor, liquid-solid, or vapor-solid, we have $f = 2$, so that there is only one degree of freedom, $\mathrm{F} = 1$: pressure and temperature cannot be chosen independently, but are dependent. The sole equilibrium condition $\mu^1\,(p,T) = \mu^2\,(p,T)$ defines the saturation pressure $p_{\mathrm{sat}}\,(T)$.

For three phases to coexist, we have $f = 3$, so that $\mathrm{F} = 0$: this is possible only at one pair of values $(p,T)_{tr}$—the triple point.

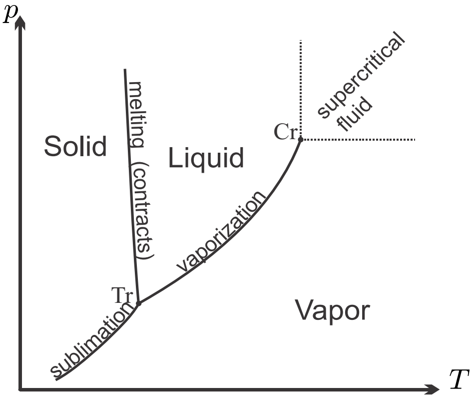

Fig. 22.1 p-T-diagram of a single substance

Figure 22.1 shows again a sketch of the p-T-diagram of a single substance (for water, actually) with the saturation curves and the triple point.

22.3 Liquid-Vapor-Mixtures: Idealized Raoult's Law

We study vapor-liquid equilibrium in mixtures where we denote the liquid phase by $'$ and the vapor phase by $''$. The Gibbs phase rule for this case reads

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[1] Just count the equal signs in each of the equations (22.2).

$$\bar{\mu}'_\alpha\left(T,p,X'_\beta\right)=\bar{\mu}''_\alpha\left(T,p,X''_\beta\right)\quad,\quad \alpha=1,\ldots,\nu\,. \tag{22.4}$$

Our goal is to simplify the phase rule by using constitutive equations for incompressible liquids and ideal gases, respectively. Deviations from this idealized behavior will be studied later. In particular, we make the following assumptions:

1. The liquids are ideal mixtures, so that

$$\bar{\mu}'_\alpha\left(T,p,X'_\beta\right)=\bar{g}'_\alpha\left(T,p\right)+\bar{R}T\ln X'_\alpha\;; \tag{22.5}$$

$\bar{g}'_\alpha\left(T,p\right)$ denotes the Gibbs free energy of α alone at (T,p) in the liquid state.

2. The pure liquids are incompressible, so that

$$\bar{g}'_\alpha\left(T,p\right)=\bar{g}'_\alpha\left(T,p^{\mathrm{sat}}_\alpha\left(T\right)\right)+v'_\alpha\left(p-p^{\mathrm{sat}}_\alpha\left(T\right)\right)\;. \tag{22.6}$$

The above results from Taylor expansion in pressure, with $\left(\frac{\partial\bar{g}}{\partial p}\right)_T=\bar{v}=$ *const.*; $p^{\mathrm{sat}}_\alpha\left(T\right)$ is the saturation pressure for component α alone.

3. The vapor can be described as a mixture of ideal gases, so that, since $\bar{g}''_\alpha\left(T,p\right)=\bar{h}''_\alpha\left(T\right)-T\left[\bar{s}^{0\prime\prime}_\alpha\left(T\right)-\bar{R}\ln\frac{p}{p_0}\right]$,

$$\begin{aligned}\bar{\mu}''_\alpha\left(T,p,X''_\beta\right)&=\bar{g}''_\alpha\left(T,p\right)+\bar{R}T\ln X''_\alpha\\&=\bar{g}''_\alpha\left(T,p^{\mathrm{sat}}_\alpha\left(T\right)\right)+\bar{R}T\ln\frac{p}{p^{\mathrm{sat}}_\alpha\left(T\right)}+\bar{R}T\ln X''_\alpha\,.\end{aligned} \tag{22.7}$$

4. The mixture is sufficiently far away from the critical points of all components, so that for the components alone

$$\bar{v}'_\alpha\ll\bar{v}''_\alpha=\frac{\bar{R}T}{p^{\mathrm{sat}}_\alpha}\,. \tag{22.8}$$

When we use the four assumptions in (22.4) together with the definition of the saturation pressure of the single components, $\bar{g}'_\alpha\left(T,p^{\mathrm{sat}}_\alpha\left(T\right)\right)=\bar{g}''_\alpha\left(T,p^{\mathrm{sat}}_\alpha\left(T\right)\right)$, we find Raoult's law for ideal mixtures (François-Marie Raoult, 1830-1901)

$$X'_\alpha p^{\mathrm{sat}}_\alpha\left(T\right)=X''_\alpha p\quad,\quad\alpha=1,\ldots,\nu\,. \tag{22.9}$$

The partial pressure of α in the vapor is given by $p_\alpha=X''_\alpha p$. Raoult's law states that the amount of component α in the liquid is proportional to its partial pressure in the vapor.

22.4 Phase Diagrams for Binary Mixtures

For the case of binary mixtures in liquid-vapor equilibrium, we have $\nu=2$ and Raoult's law gives the equations

$$X_1' p_1^{\mathrm{sat}}(T) = X_1'' p \quad , \quad (1 - X_1') \, p_2^{\mathrm{sat}}(T) = (1 - X_1'') \, p \, . \tag{22.10}$$

The variables are (T, p, X_1', X_1''), and according to Gibbs' phase rule there are two degrees of freedom, $\mathrm{F} = 2$, so that when two variables are prescribed, the others are fixed.

In particular, when pressure and temperature are prescribed, the values for the mole fractions in both phases are computed as

$$X_1' = \frac{p_2^{\mathrm{sat}}(T) - p}{p_2^{\mathrm{sat}}(T) - p_1^{\mathrm{sat}}(T)} \quad , \quad X_1'' = \frac{p_1^{\mathrm{sat}}(T)}{p} \frac{p_2^{\mathrm{sat}}(T) - p}{p_2^{\mathrm{sat}}(T) - p_1^{\mathrm{sat}}(T)} \, . \tag{22.11}$$

For given temperature T, we can draw the two curves into a p-X-diagram. Solving for pressure gives the saturated liquid line,

$$p(T, X') = p_2^{\mathrm{sat}}(T) - \left(p_2^{\mathrm{sat}}(T) - p_1^{\mathrm{sat}}(T)\right) X_1' \, , \tag{22.12}$$

and the saturated vapor line,

$$p(T, X'') = \frac{p_1^{\mathrm{sat}}(T) \, p_2^{\mathrm{sat}}(T)}{(1 - X_1'') \, p_1^{\mathrm{sat}}(T) + X_1'' p_2^{\mathrm{sat}}(T)} \, . \tag{22.13}$$

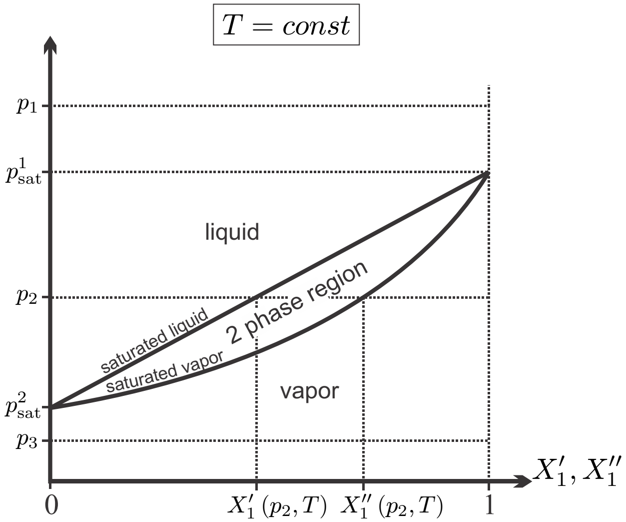

Fig. 22.2 p-X-diagram for a binary mixture at temperature T, according to Raoult's law in the idealized case

Figure 22.2 shows a p-X-diagram for fixed T with the two curves that meet for $X_1' = X_1'' = 0$ and $X_1' = X_1'' = 1$ at the respective saturation pressures. For the assumptions used, the saturated liquid curve is a straight line.

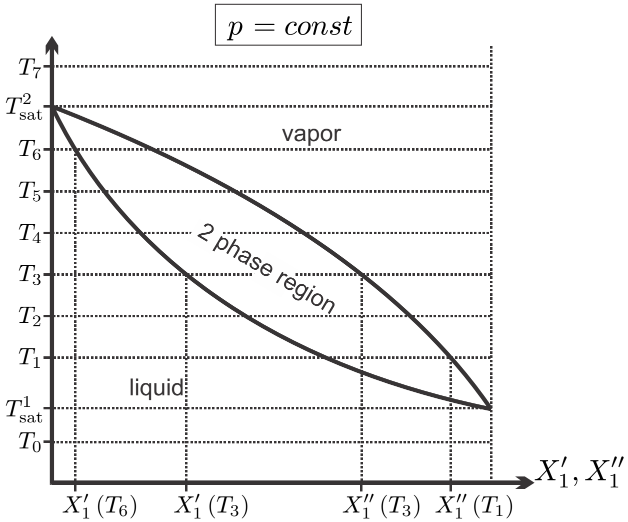

Fig. 22.3 T-X-diagram for a binary mixture at pressure p, according to Raoult's law in the idealized case

Also indicated in the figure are three pressures. At p_1 the pressure is higher than both saturation pressures, and the there is only one single liquid phase. At p_3 the pressure is lower than both saturation pressures, and there is only one single vapor phase. At the intermediate pressure p_2, which lies between the two saturation pressures, the mixture can be found either as pure liquid or pure vapor phase, or it can split into two phases. What happens depends on the overall mole fraction of the mixture $X_1 = \frac{n_1'+n_1''}{n_1'+n_1''+n_2'+n_2''}$. If $X_1 \leq X_1'(p_2, T)$, there is only a single liquid phase, and for $X_1 \geq X_1''(p_2, T)$, there is only a single vapor phase. If $X_1'(p_2, T) < X_1 < X_1''(p_2, T)$, the mixture splits into two phases, the liquid phase with mole fraction $X_1'(p_2, T)$ and the vapor phase with mole fraction $X_1''(p_2, T)$. The component with the larger vapor pressure (here component 1) is more volatile, i.e. more keen to evaporate, and the vapor is richer in the more volatile component while the liquid is depleted of it.

The equations (22.12, 22.13) can be numerically solved for T; this requires equations or tables for the saturation pressures $p_\alpha^{\rm sat}(T)$. The resulting T-X-diagram for constant pressure is sketched in Fig. 22.3. The interpretation of the diagram follows the same lines as for the p-X-diagram: For temperatures above both saturation temperatures $T_\alpha^{\rm sat}(p)$, e.g., T_7, the mixture will be pure vapor for all values X_1. The mixture will be pure liquid for temperatures below both saturation temperatures, e.g., T_0 in the figure. For temperatures between the two saturation temperatures (T_1 to T_6), the mixture will split into two phases at $X_1'(T, p)$ and $X_1''(T, p)$, if the overall mole fraction X_1 lies between these values; else the mixture is either liquid (for $X_1 \leq X_1'(T,p)$) or vapor (for $X_1 \geq X_1''(T,p)$).

22.5 Distillation

Distillation is a separation procedure based on the different compositions of vapor and liquid mixture in equilibrium. Figure 22.4 shows a sketch for a bubble tray column for distillation that matches the T-X-diagram of Fig. 22.3. A temperature gradient is imposed by heating at the bottom and cooling at the top of the column. Several bubble trays are inserted in the column. Industrial columns have up to 100 trays and can reach heights of 60 metres. Heating at the bottom generates vapor that rises in the column, while liquid is generated by condensation at the cooled top and drips down.

On the trays, which all have different temperatures following the temperature gradient established in the column, the rising vapor passes as bubbles through the liquid. This contact between vapor and liquid establishes thermodynamic equilibrium on the tray, determined by the pressure in the column and the temperature on the tray. Consider the tray at T_3: The vapor leaving the tray upwards has the mole fraction $X_1''(T_3)$ while the liquid dripping down has the mole fraction $X_1'(T_3)$. Figure 22.5 illustrates how liquid and vapor pass through the tray: The vapor is forced to bubble through the liquid, and this leads to exchange of components and energy.

For the mixture shown in Figs. 22.3 and 22.4, component 1 is more volatile, so that the vapor becomes richer in component 1 as it ascends, while the liquid becomes richer in component 2 as it descends.

The design and dimensioning of distillation columns is the task of chemical engineers and will not be discussed further. Obviously, distillation becomes more complex when multicomponent mixtures are involved, when saturation temperatures of components are close, and when the mixtures exhibit non-ideal behavior, e.g., azeotropes, see Sec. 22.11.

22.6 Saturation Pressure and Temperature of a Solvent

We consider solutions of low volatility components, e.g., salts, in a more volatile solvent, e.g., water, in liquid-vapor equilibrium. The mole fraction of solvent vapor is

$$X_\nu'' = 1 - \sum_{\alpha=1}^{\nu-1} X_\alpha'' = 1 - \sum_{\alpha=1}^{\nu-1} X_\alpha' \frac{p_\alpha^{\mathrm{sat}}(T)}{p} , \tag{22.14}$$

where we used Raoult's law for the mole fractions of the dissolved components, X_α''. For the non-volatile substances the saturation pressures $p_\alpha^{\mathrm{sat}}(T)$

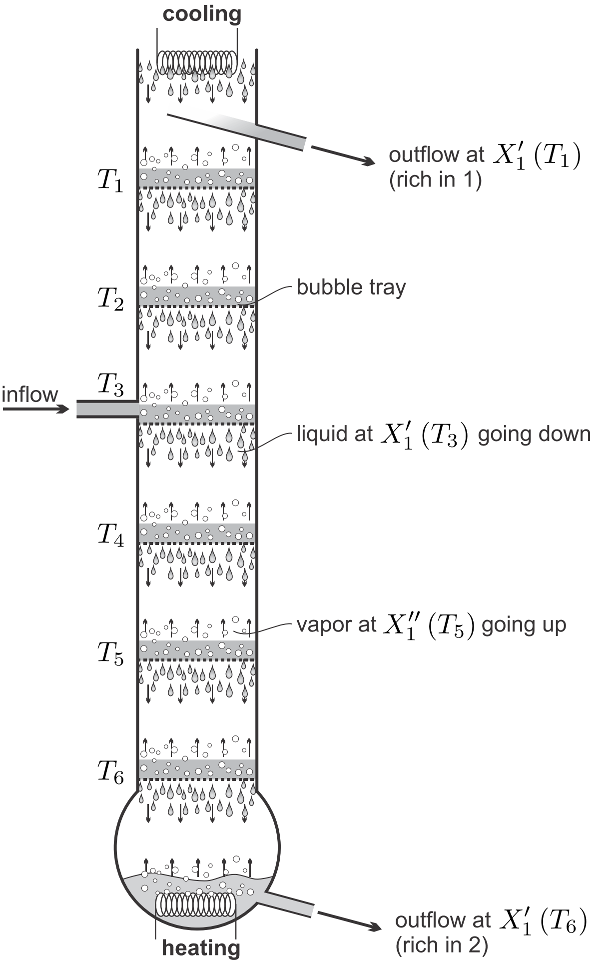

Fig. 22.4 Bubble-tray distillation column

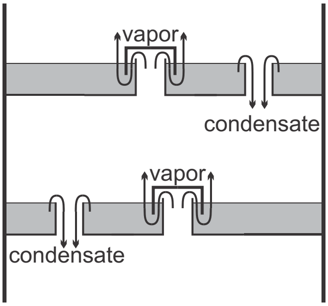

Fig. 22.5 Schematic close-up of bubble trays

are very low, so that $\sum_{\alpha=1}^{\nu-1} X'_\alpha \frac{p_\alpha^{\text{sat}}(T)}{p} \ll 1$; accordingly we can approximate $X''_\nu \simeq 1$. Raoult's law (22.9) for the solvent, $X''_\nu p = X'_\nu p_\nu^{\text{sat}}(T)$, then simplifies to

$$p_{\text{sol}}(T) = X'_\nu p_\nu^{\text{sat}}(T) \ . \tag{22.15}$$

Here, $p_{\text{sol}}(T)$ denotes the actual saturation pressure of the solvent vapor over the solution at temperature T. In other words, the ideal mixture of composition X'_ν at temperature T will boil when the pressure is $p_{\text{sol}}(T)$.

According to (22.15) the actual pressure in the solvent vapor, p_{sol}, is smaller than the saturation pressure of the solvent alone, $p_\nu^{\text{sat}}(T)$, that is the dissolved substances reduce the volatility of the solvent. The reason for this is a competition between solvent vapor and the salt dissolved in the liquid to increase their entropy: The solvent vapor has a larger entropy than the solvent liquid, but the dissolved salt has a larger entropy when it can access a larger volume, that is when there is more liquid solvent.

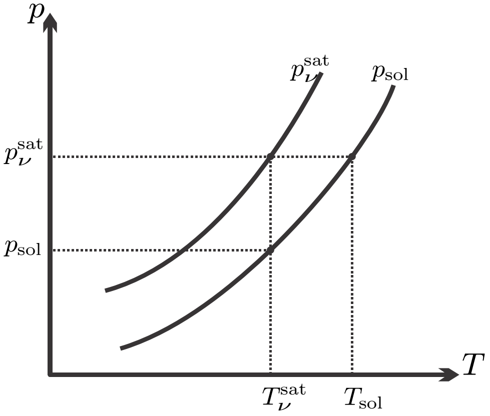

Fig. 22.6 p-T-diagram: saturation curve for pure solvent and for solution

Figure 22.6 shows the saturation curves for the pure solvent and the solution in a p-T-diagram. The curve for the pure solvent (p_ν^{sat}) lies above the curve for the solution (p_{sol}), in accordance with (22.15). The figure shows that for a given pressure p the saturation temperature $T_{\text{sol}}(p)$ of the solution is higher than the saturation temperature $T_\nu^{\text{sat}}(p)$ of the solvent alone: at a given pressure saltwater boils at higher temperatures than pure water. To estimate the change in saturation temperature, we assume that the slope of the new saturation curve is close to the slope of the saturation curve of the solvent as described by the Clausius-Clapeyron equation (17.46), that is

$$\frac{T_{\text{sol}} - T_\nu^{\text{sat}}}{p_\nu^{\text{sat}} - p_{\text{sol}}} \simeq \frac{dT_\nu^{sat}}{dp} = T_\nu^{sat} \frac{v''_\nu - v'_\nu}{h_{LV}} \ . \tag{22.16}$$

With the assumptions that the liquid volume can be neglected against the vapor volume, and that the vapor follows the ideal gas law, and with (22.15), this yields

$$T_{\mathrm{sol}} - T_\nu^{\mathrm{sat}}(p) = \frac{R_\nu \left[T_\nu^{sat}(p)\right]^2}{h_{LV}(p)} \left(1 - X'_\nu\right) \ . \tag{22.17}$$

T_{sol} is the temperature at which an ideal mixture of composition X'_ν at pressure p will boil.

22.7 Freezing of a Liquid Solution

Ice crystals cannot easily accept salt molecules into their lattice, and thus when a salt solution is cooled, first water will freeze out, while the salt will remain in the liquid as long as possible. Sea-ice, that is ice that freezes out of oceans in cold climates, contains no salt. As sea-ice forms, the salt content of the water just below the ice increases. This salty water has increased density, and will sink towards the bottom of the ocean, thus driving ocean currents. Completely frozen salt-water solution is a mixture of pure ice and regions of salt-water crystals, e.g., NaCl-$2H_2O$ crystals.

The dissolved salt ions move in the liquid, they have a larger entropy when they can move in a larger volume, that is when more liquid water is present. So in order to gain entropy, the dissolved salt prevents water from freezing, which is observed as a drop in the temperature at which water will freeze. To estimate this drop, we consider solid and liquid as incompressible ideal mixtures, so that we can approximate the chemical potentials of the solvent in liquid solution ($'$) and ice ($''$) as

$$\mu'_\nu = g'_\nu\left(T, p_\nu^{\mathrm{sat}}(T)\right) + v'_\nu\left(p_{\mathrm{melt}} - p_\nu^{\mathrm{sat}}(T)\right) + R_\nu T \ln X'_\nu \ , \tag{22.18}$$

$$\mu''_\nu = g''_\nu\left(T, p_\nu^{\mathrm{sat}}(T)\right) + v''_\nu\left(p_{\mathrm{melt}} - p_\nu^{\mathrm{sat}}(T)\right) + R_\nu T \ln X''_\nu \ . \tag{22.19}$$

With no salt in the ice, we have $X''_\nu = 1$, and equating the chemical potentials, $\mu'_\nu = \mu''_\nu$, gives

$$p_{\mathrm{melt}}(T) - p_\nu^{\mathrm{sat}}(T) = -\frac{R_\nu T}{v'_\nu - v''_\nu} \ln X'_\nu \ . \tag{22.20}$$

For water, the volume of ice is larger than the volume of liquid, $v'_\nu - v''_\nu < 0$, and hence the melting pressure of the solution, $p_{\mathrm{melt}}(T)$, is lower than that of pure water ($p_\nu^{\mathrm{sat}}(T)$).

To compute the change in melting temperature, we use Fig. (22.7) and the Clausius-Clapeyron equation to estimate

$$\frac{T_v^{\mathrm{sat}}(p) - T_{\mathrm{melt}}(p)}{p_{\mathrm{melt}}\left(T_v^{\mathrm{sat}}\right) - p_\nu^{\mathrm{sat}}\left(T_v^{\mathrm{sat}}\right)} \simeq \frac{dT_v^{\mathrm{sat}}}{dp} = T_v^{\mathrm{sat}} \frac{v''_\nu - v'_\nu}{h''_\nu - h'_\nu} \ , \tag{22.21}$$

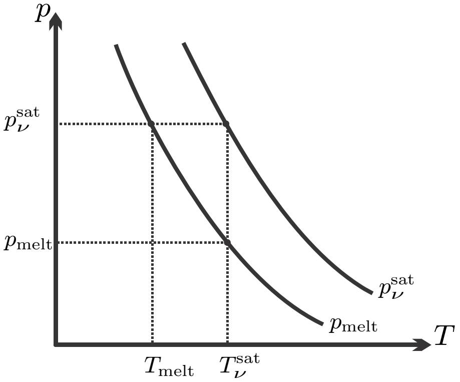

Fig. 22.7 p-T-diagram: melting curve for pure solvent and for solution

so that, with (22.20),

$$T_{\text{melt}}(p) - T_v^{\text{sat}}(p) = \frac{R_\nu \left[T_v^{\text{sat}}\right]^2}{h'_\nu - h''_\nu} \ln X'_\nu < 0 \,. \tag{22.22}$$

Here, $h'_\nu - h''_\nu$ is the heat of melting, e.g., $h'_\nu - h''_\nu = 333.7 \frac{\text{kJ}}{\text{kg}}$ for water at $0\,°\text{C}$.

22.8 Non-ideal Mixtures: Activity and Fugacity

So far, we considered only ideal mixtures. In this section, we study how non-ideal effects are incorporated into the description.

The activity coefficient $\gamma_\alpha(T, p, X_\beta)$ and the activity $a_\alpha(T, p, X_\beta) = \gamma_\alpha(T, p, X_\beta)\, X_\alpha$ are defined such that the chemical potential reads

$$\bar{\mu}_\alpha(T, p, X_\beta) = \bar{g}_\alpha(T, p) + \bar{R}T \ln a_\alpha = \bar{g}_\alpha(T, p) + \bar{R}T \ln\left[\gamma_\alpha X_\alpha\right] \,. \tag{22.23}$$

As always, $\bar{g}_\alpha(T, p)$ denotes the Gibbs free energy of component α alone, under the same pressure and temperature as the mixture. For ideal mixtures or ideal gases, the activity coefficient reduces to $\gamma_\alpha = 1$, and the activity becomes $a_\alpha = X_\alpha$.

For the description of vapors, one uses typically the fugacity coefficient $\varphi_\alpha(T, p, X_\beta)$ and the fugacity $f_\alpha(T, p, X_\beta) = \varphi_\alpha X_\alpha \frac{p}{p_\alpha^{\text{sat}}(T)}$, which are defined such that

$$\begin{aligned} \bar{\mu}_\alpha(T, p, X_\beta) &= \bar{g}_\alpha\left(T, p_\alpha^{\text{sat}}(T)\right) + \bar{R}T \ln f_\alpha \\ &= \bar{g}_\alpha\left(T, p_\alpha^{\text{sat}}(T)\right) + \bar{R}T \ln\left[\varphi_\alpha X_\alpha \frac{p}{p_\alpha^{\text{sat}}(T)}\right] \,. \end{aligned} \tag{22.24}$$

Here, $\bar{g}_\alpha\left(T, p_\alpha^{\text{sat}}(T)\right)$ denotes the Gibbs free energy of component α alone at saturation under the same temperature as the mixture. When the vapor can be described as an ideal gas, the fugacity coefficient reduces to $\varphi_\alpha = 1$.

Just as the chemical potential, activity and fugacity depend on the detailed composition, X_β, of the respective phase. Thus, on the first glance, it might seem that the introduction of activity and fugacity and their coefficients has no advantage, since one replaces one unknown function, the chemical potential, with another, activity or fugacity. The latter, however, are accessible to measurements, and this is why they are used in chemical engineering.

To understand how fugacity can be measured, we consider the Gibbs equation (20.1) and take mixed derivatives with respect to p and n_α, to find

$$\frac{\partial^2 G}{\partial p \partial n_\alpha} = \left(\frac{\partial \bar{\mu}_\alpha}{\partial p}\right)_{T, n_\alpha, n_\beta} = \left(\frac{\partial V}{\partial n_\alpha}\right)_{T, p, n_\beta} = \frac{\partial^2 G}{\partial n_\alpha \partial p} \,. \tag{22.25}$$

Here, we insert the chemical potential in the form (22.24) and separate the term containing the fugacity φ_α. The result is an expression for the change of φ_α with pressure,

$$\left(\frac{\partial \ln \varphi_\alpha}{\partial p}\right)_{T, n_\alpha, n_\beta} = \frac{1}{\bar{R}T}\left(\frac{\partial V}{\partial n_\alpha}\right)_{T, p, n_\beta} - \frac{1}{p} \,. \tag{22.26}$$

In the limit $p \to 0$ the vapor will behave as an ideal gas, and therefore will have the fugacity coefficient $\varphi_\alpha\left(T, p = 0, X_\beta\right) = 1$. Integration at constant temperature between $p = 0$ and the actual pressure p thus gives the fugacity coefficient as

$$\ln \varphi_\alpha\left(T, p, X_\beta\right) = \frac{1}{\bar{R}T} \int_{p=0}^{p} \left[\left(\frac{\partial V}{\partial n_\alpha}\right)_{T, p', n_\beta} - \frac{\bar{R}T}{p'}\right] dp' \,. \tag{22.27}$$

The function under the integral can be measured by systematically adding component α, and determining the resulting volume change; this must be repeated for many pressures. Thus, the fugacity can be measured in the vapor phase.

Measurements of activity and activity coefficients rely on Raoult's law. We reconsider Raoult's law for the equilibrium between a liquid and a vapor mixture, where we now use activity and fugacity coefficients to describe the liquid and the vapor, respectively. Gibbs' phase rule $\bar{\mu}'_\alpha\left(T, p, X'_\beta\right) = \bar{\mu}''_\alpha\left(T, p, X''_\beta\right)$ becomes

$$\bar{g}'_\alpha(T, p) + \bar{R}T \ln a'_\alpha = \bar{g}''_\alpha\left(T, p_\alpha^{\text{sat}}(T)\right) + \bar{R}T \ln f''_\alpha \,. \tag{22.28}$$

When we consider the liquid as almost incompressible, and assume that its molar volume can be ignored compared to the molar volume of the vapor,[2]

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[2] The same assumptions were used in Sec. 22.3.

this reduces to

$$a'_\alpha = f''_\alpha \quad \text{or} \quad \gamma'_\alpha X'_\alpha = \varphi''_\alpha X''_\alpha \frac{p}{p_\alpha^{\text{sat}}(T)} \,. \tag{22.29}$$

It follows that activity can be measured when fugacity is known.

22.9 A Simple Model for Heat of Mixing and Activity

Ideal mixtures have zero enthalpy of mixing H_{mix}, and their activity coefficients are unity. We shall now develop a simple model for H_{mix} to describe non-ideal behavior. We consider binary mixtures only.

Part of the internal energy of a substance comes from the interaction potential between neighboring molecules. For a component alone, this contribution to energy is included in enthalpy $\bar{h}_\alpha(T,p)$ or free energy $\bar{g}_\alpha(T,p)$, and we can consider identical neighboring particles as energetically neutral.

In a mixture between components 1 and 2, there will be neighboring pairs of the same type (1-1, 2-2) and pairs of different type (1-2). While the former are energetically neutral, the formation of the latter can either release or require energy. When the attractive force between different particles (1-2) is stronger than that between equal particles (1-1, 2-2), 1-2 pairs are energetically preferred over neutral pairs, due to negative interaction energy; then energy is released when a mixed pair (1-2) is formed. When the attractive force between different particles (1-2) is weaker than between equal particles (1-1, 2-2), neutral pairs are energetically preferred over (1-2) pairs, due to positive interaction potential; then energy is required to form a pair.

We consider a mixture of $N = N_1 + N_2$ particles of types 1, 2. The probability to find a particle of type α is $\frac{N_\alpha}{N}$ and thus the probability to find a pair (1-2) is proportional to $\frac{N_1 N_2}{N^2}$. The total number of pairs is of the order of the total number of particles N, and thus the number of (1-2) pairs is proportional to $N\frac{N_1 N_2}{N^2} = \frac{N_1 N_2}{N}$. When we introduce mole numbers, the enthalpy of mixing is

$$H_{\text{mix}} = \bar{\varepsilon}\frac{n_1 n_2}{n_1 + n_2} \quad , \quad \bar{\varepsilon} \gtrless 0 \,. \tag{22.30}$$

Depending on its sign, $\bar{\varepsilon}$ is the energy released or required to form one mole of (1-2) pairs.

With the entropy of mixing as before, the Gibbs free energy (20.34) of the binary mixture becomes

$$G = n_1 \bar{g}_1(T,p) + n_2 \bar{g}_2(T,p) + \bar{\varepsilon}\frac{n_1 n_2}{n_1 + n_2} + \bar{R}T\left(n_1 \ln\frac{n_1}{n_1+n_2} + n_2 \ln\frac{n_2}{n_1+n_2}\right) \,. \tag{22.31}$$

The chemical potential is the derivative of the total Gibbs free energy (20.2),

$$\bar{\mu}_\alpha = \left(\frac{\partial G}{\partial n_\alpha}\right)_{T,p,n_\beta} = \bar{g}_\alpha\left(T,p\right) + \bar{\varepsilon}\left(1 - X_\alpha\right)^2 + \bar{R}T\ln X_\alpha \,. \tag{22.32}$$

Comparison with (22.23) gives the activity coefficient as

$$\gamma_\alpha = \exp\left[\frac{\bar{\varepsilon}}{\bar{R}T}\left(1 - X_\alpha\right)^2\right] \,. \tag{22.33}$$

22.10 Gas Solubility: Henry's Law

We consider phase equilibrium between a liquid non-ideal mixture with the activity coefficient from the model of the previous section, and an ideal gas vapor phase (fugacity coefficient $\varphi''_\alpha = 1$). Then, with the activity coefficient (22.33), Raoult's law (22.29) assumes the form

$$\exp\left[\frac{\bar{\varepsilon}}{\bar{R}T}\left(1 - X'_\alpha\right)^2\right] X'_\alpha = \frac{p''_\alpha}{p^{\text{sat}}_\alpha\left(T\right)} \,, \tag{22.34}$$

where $p''_\alpha = X''_\alpha p$ is the partial pressure of α in the vapor.

We consider a not too volatile liquid solvent, say water, under an atmosphere of volatile vapors, say air, where we can expect that the mole fractions of air components (oxygen, nitrogen, argon, ...) in the liquid are rather small. Then, in the above, we can set $\left(1 - X'_\alpha\right)^2 \simeq 1$, and find the mole fraction of gases dissolved in the liquid given by Henry's law (William Henry, 1774-1836),

$$X'_\alpha = \frac{p''_\alpha}{p^{\text{sat}}_\alpha\left(T\right)\exp\left[\frac{\bar{\varepsilon}}{\bar{R}T}\right]} = \frac{p''_\alpha}{H_\alpha\left(T\right)} \,, \tag{22.35}$$

with Henry's constant $H_\alpha\left(T\right)$. The saturation pressure can be approximated by (17.48), so that Henry's constant becomes[3]

$$H_\alpha\left(T\right) = H_\alpha\left(T_0\right)\exp\left[\mathit{\Delta} H_\alpha\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad \text{with} \quad \mathit{\Delta} H_\alpha = \frac{\bar{h}^{LV}_\alpha - \bar{\varepsilon}}{\bar{R}} \,. \tag{22.36}$$

For oxygen, nitrogen, and carbon dioxide the following data can be found ($T_0 = 298\,\text{K}$):

$$\begin{aligned} H_{\text{O}_2}\left(T_0\right) &= 43102\,\text{bar} \quad , \quad \mathit{\Delta} H_{\text{O}_2} = 1700\,\text{K} \,, \\ H_{\text{N}_2}\left(T_0\right) &= 85590\,\text{bar} \quad , \quad \mathit{\Delta} H_{\text{N}_2} = 1300\,\text{K} \,, \\ H_{\text{CO}_2}\left(T_0\right) &= 1648\,\text{bar} \quad , \quad \mathit{\Delta} H_{\text{CO}_2} = 2400\,\text{K} \,, \\ H_{\text{He}}\left(T_0\right) &= 149700\,\text{bar} \quad , \quad \mathit{\Delta} H_{\text{He}} = 230\,\text{K} \,. \end{aligned}$$

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[3] Rolf Sander: Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, `http://www.henrys-law.org/`

It should be noted that at environmental temperatures oxygen and nitrogen are well above their critical point, where no saturation pressure exists. Therefore, it is somewhat surprising that the above derivation gives a meaningful result for these temperatures.

In carbonated drinks, carbon dioxide dissolves in water under pressure (normally around 2 bar, depending on temperature). When the pressure is released by opening the bottle or can, the gas bubbles out, to establish the equilibrium for the partial pressure of CO_2 at the surface. From (22.36) we see that Henry's constant grows with temperature, so that less gas is dissolved in warmer water. This is the reason for the effervescence of a warm pop can as compared to a cold one.

Guinness beer is nitrogenated with a special tab. Due to the low dissolution of N_2, bottling it would give a very flat beer (under the same pressure one could dissolve 50 times more CO_2 than N_2), unless a "widget" is used, where N_2 is enclosed in a small capsule that releases the gas when the pressure in the can drops after it is opened.

Colder oceans are richer in oxygen, and thus are rich in marine life. Therefore big whales migrate between the polar waters where they find most food.

For the solvent, the mole fraction in the liquid is almost unity, $X'_\nu \simeq 1$, which implies that the activity coefficient is close to unity as well, $\gamma'_\nu = \exp\left[\frac{\bar{\varepsilon}}{\bar{R}T}\left(1 - X'_\nu\right)^2\right] \simeq 1$. Hence, evaluation of Raoult's law gives $p^{\mathrm{sat}}_\alpha\left(T\right) = p''_\alpha$, i.e., the partial pressure of water in a saturated water-air mixture is, for all practical applications, equal to the saturation pressure of water, as used in the discussion of psychrometrics.

22.11 Phase Diagrams with Azeotropes

Next, we study phase diagrams for non-ideal mixtures, based on Raoult's law (22.29). To obtain interesting behavior, it suffices to consider non-ideality in the liquid phase, expressed through activity coefficients of the form (22.33), while the vapor is considered as a mixture of ideal gases where the fugacity coefficients are unity.

For a binary mixture, we obtain the two equations (with $X_2 = 1 - X_1$),

$$X''_1 p = p''_1\left(T, X'_1\right) = p^{\mathrm{sat}}_1\left(T\right) X'_1 \exp\left[\frac{\bar{\varepsilon}}{\bar{R}T}\left(1 - X'_1\right)^2\right], \quad (22.37)$$

$$\left(1 - X''_1\right) p = p''_2\left(T, X'_1\right) = p^{\mathrm{sat}}_2\left(T\right)\left(1 - X'_1\right) \exp\left[\frac{\bar{\varepsilon}}{\bar{R}T} X'^2_1\right]. \quad (22.38)$$

Note that, as indicated, the left hand sides are just the partial pressures in the vapor, expressed through the right hand sides as functions of temperature and liquid composition.

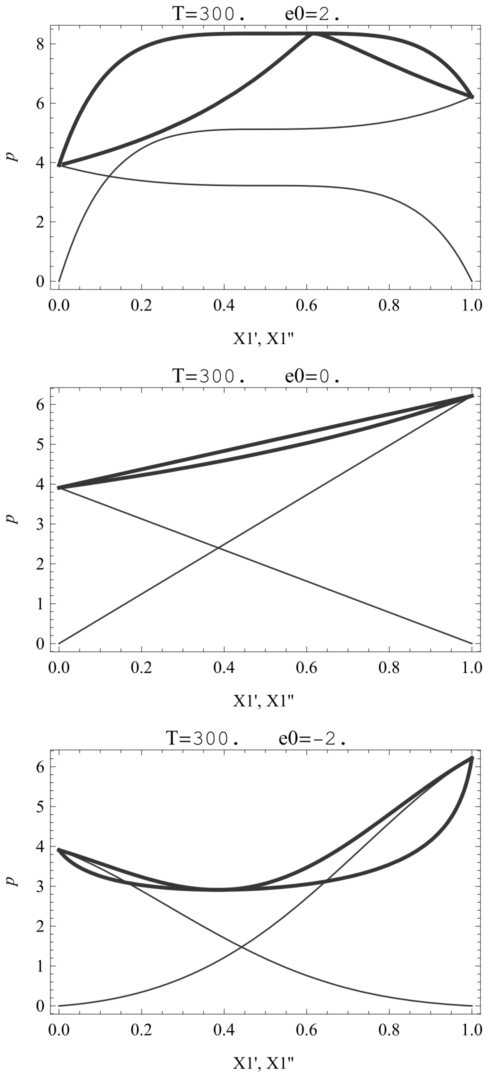

Fig. 22.8 p-X-digrams for ideal and non-ideal mixtures. Bold curves: saturated liquid and saturated vapor lines. Thin curves: partial vapor pressures $p''_\alpha(T, X'_1)$.

The saturated liquid curve is obtained from adding both equations to eliminate X''_1,

$$p\left(T, X'_1\right) = p_1^{\mathrm{sat}}\left(T\right) X'_1 \exp\left[\frac{\bar{\varepsilon}}{\bar{R}T}\left(1 - X'_1\right)^2\right] + p_2^{\mathrm{sat}}\left(T\right)\left(1 - X'_1\right) \exp\left[\frac{\bar{\varepsilon}}{\bar{R}T} X'^2_1\right] . \tag{22.39}$$

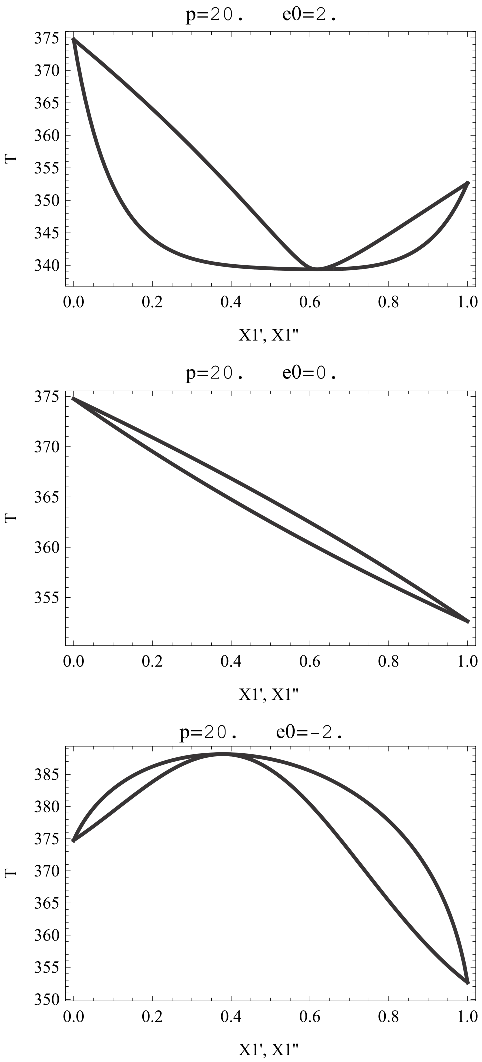

Fig. 22.9 T-X-digrams for ideal and non-ideal mixtures

The saturated vapor curve $p\left(T, X_1''\right)$ cannot be computed analytically, since it is not possible to analytically eliminate X_1' from the equations. Instead, we obtain it as follows: Division of the two equations for p_1'' and p_2'' gives

$$X_1''\left(T, X_1'\right) = \frac{1}{1 + \frac{p_2^{\mathrm{sat}}(T)}{p_1^{\mathrm{sat}}(T)} \left(\frac{1}{X_1'} - 1\right) \exp\left[-\frac{\bar{\varepsilon}}{RT}\left(1 - 2X_1'\right)\right]} \,. \tag{22.40}$$

With this, the saturated vapor curve can be expressed in parametric form as

$$\left\{p\left(T,X_1'\right),X_1''\left(T,X_1'\right)\right\} \tag{22.41}$$

with X_1' as curve parameter.[4]

Figure 22.8 shows the phase diagrams together with the vapor pressures $p_\alpha''\left(T,X_1'\right)=X_\alpha''p$ for various values of $\bar{\varepsilon}$, based on data given in problem 22.25. For non-ideal mixtures, the saturated liquid and vapor lines meet not only for the pure substances ($X_1=1$ or $X_1=0$), but also in a point between, the so-called azeotrope.

The corresponding T-X-diagrams at constant p, which are of importance to understand distillation processes, can be constructed as follows: For the saturated liquid line one prescribes $\left(X_1',p\right)$ in (22.39) and solves numerically for T to find one point $\left(X_1',T\right)$ of the saturated liquid curve $T\left(p,X_1'\right)$. The curve results from repetition for many values X_1'. For the saturated vapor curve one evaluates (22.40) for values on the saturated liquid curve to compute $X_1''\left(T\left(p,X_1'\right),X_1'\right)$ and then uses the saturated liquid line to find points on the saturated liquid lines as $\left\{T\left(p,X_1'\right),X_1''\left(T\left(p,X_1'\right),X_1'\right)\right\}$. Figure 22.9 shows the resulting T-X-diagrams corresponding to the p-X-diagrams above, they show azeotropes as well.

As compared to the ideal mixture, when the formation of mixed pairs (1-2) is not favored, which is the case for $\bar{\varepsilon}>0$, the mixture becomes more volatile, as can be seen from the larger vapor pressures in Fig. 22.8 and the lower saturation temperatures in Fig. 22.9. When the formation of mixed pairs is favored, $\bar{\varepsilon}<0$, the mixture is less volatile, vapor pressures are lower, and saturation temperatures are higher.

Azeotropic mixtures cannot be separated by distillation processes, as becomes obvious when one considers the distillation column discussed earlier in conjunction with an azeotropic T-X-diagram. The location of the azeotrope might change with pressure, and separation can be achieved by distillation at different pressures (for the model used to generate these figures, this effect is very weak, however). Other methods for separation of azeotropic mixtures are discussed in the chemical engineering literature.

Problems

22.1. Ammonia and Water

Absorption refrigeration systems often employ two phase equilibrium mixtures of ammonia (NH_3) and water (H_2O). For the following problems, assume an ideal mixture:

1. A liquid-vapor mixture of ammonia and water at 30 °C has a mole fraction of ammonia in the liquid of 60%. Determine the mole fractions of water

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[4] In other words, for given T, for each value X_1' one finds a point $\left\{p\left(T,X_1'\right),X_1''\left(T,X_1'\right)\right\}$ of the saturated vapor curve in the p-X-diagram.

and ammonia in the vapor phase, and the total pressure of the mixture. Saturation pressure of NH_3 at $p_{\text{sat}}(30\,^\circ\text{C}) = 1116.5\,\text{kPa}$.
2. A two-phase mixture of ammonia and water is in equilibrium at $50\,^\circ\text{C}$. The composition of the vapor phase is 99 percent NH_3 and 1 percent H_2O by mole numbers. Determine the composition of the liquid phase and the total pressure. Saturation pressure of NH_3 at $50\,^\circ\text{C}$ is $2033.5\,\text{kPa}$.
3. A liquid-vapor mixture of ammonia and water is at $40\,^\circ\text{C}$ and $1000\,\text{kPa}$. Determine the mole fractions of water and ammonia in the vapor and liquid phase. Saturation pressure of NH_3 at $p_{\text{sat}}(40\,^\circ\text{C}) = 1554.33\,\text{kPa}$.
4. A liquid-vapor mixture of ammonia and water is in equilibrium at $10\,^\circ\text{C}$ and $500\,\text{kPa}$. Determine the mole fractions of water and ammonia in the vapor and liquid phase. Saturation pressure of NH_3: $p_{\text{sat}}(10\,^\circ\text{C}) = 615.29\,\text{kPa}$.

22.2. Binary Mixture of Propane and 1-Butane I

Consider a mixture of $n_1 = 200\,\text{kmol}$ propane (C_3H_8) and $n_2 = 100\,\text{kmol}$ 1-butane (C_4H_{10}), with pressure $p = 10\,\text{bar}$ at a temperature of $320\,\text{K}$. The saturation pressures of the pure substances are $p_1^{\text{sat}}(320\,\text{K}) = 15.722\,\text{bar}$, and $p_2^{\text{sat}}(320\,\text{K}) = 4.537\,\text{bar}$.

1. Use the idealized Raoult law to find the mole fractions X_1', X_1''.
2. Determine the mole numbers n_1', n_2', n_1'', n_2'' .

22.3. Binary Mixture of Propane and 1-Butane II

Consider a mixture of $n_1 = 25\,\text{kmol}$ propane (C_3H_8) and $n_2 = 100\,\text{kmol}$ 1-butane (C_4H_{10}), at $T = 350\,\text{K}$ and $p = 12\,\text{bar}$. The saturation pressures of the pure substances can be found from the Antoine equation $\ln p_{\text{sat}}(T) = A - \frac{B}{C+T}$, where the pressure is measured in bars, the temperature in K, and the constants have the values

	A	B	C
C_3H_8	9.1058	1872.46	-25.16
C_4H_{10}	9.0580	2154.9	-34.42

1. Use the idealized Raoult law to find the mole fractions X_1', X_1''.
2. Determine the mole numbers n_1', n_2', n_1'', n_2'' .

22.4. Binary Mixture of Propane and 1-Butane III

Consider a two phase mixture of $n_1 = 150\,\text{kmol}$ propane (C_3H_8) and an unknown amount n_2 of butane (C_4H_{10}), at a temperature of $320\,\text{K}$.

At $p = 10\,\text{bar}$ the mole fraction of propane in the liquid phase is $X_1' = 0.488$, and the amount of propane in the liquid phase is $75\,\text{kmol}$.

The saturation pressure of propane is $p_{\text{sat},1}(320\,\text{K}) = 15.7\,\text{bar}$.

1. Use the idealized Raoult law to find the mole fraction X_1''.
2. Determine the mole numbers n_2', n_1'', n_2''.
3. Determine the saturation pressure of butane at $320\,\text{K}$.

22.5. Binary Mixture of Propane and 1-Butane IV

Consider an ideal two phase mixture of propane (C_3H_8) and butane (C_4H_{10}), at temperature of 330 K. At this temperature, the saturation pressures of propane and butane are 19.4 bar and 5.86 bar, respectively. The mixture is equimolar, with 220 kmol of each component present, and the mole fraction of butane in the vapor phase is 30%.

1. Determine the mole fractions of butane and propane in both phases.
2. Determine the pressure of the mixture, p .
3. Determine the total mole number in the liquid.

22.6. Phase Diagrams for Propane and 1-Butane

Construct phase diagrams for a mixture of propane and 1-butane (ideal mixture). Use a computer with suitable software for plotting and evaluating of equations.

The saturation pressures of the pure substances can be found from the Antoine equation $\ln p_{\mathrm{sat}}(T) = A - \frac{B}{C+T}$ with

	A	B	C
C_3H_8	9.1058	1872.46	-25.16
C_4H_{10}	9.0580	2154.9	-34.42

where the pressure is measured in bar, and the temperature in K.

1. Construct and plot the p-X phase diagram for a variety of temperatures (stay in between critical and triple points!).
2. Construct and plot the T-X diagram for a variety of pressures.

22.7. Water and R134a

Mixtures of water and refrigerant are used in self-foaming products. Consider a mixture of 120 g R134a (molar mass $102\frac{\mathrm{g}}{\mathrm{mol}}$) and 50 g water, initially at 20 °C and 2 bar, later at 20 °C and 1 bar.

1. Find the overal mole fraction of R134a in the mixture.
2. Find the mole fractions X'_R, X''_R, X'_W, X''_W for both pressures. Use the idealized Raoult law.
3. Draw a p-X-diagram for the mixture, and indicate the two states and the overall mole fraction in the diagram. Carefully consider whehter the mixture is all liquid, liquid-vapor mix, or all vapor.
4. Determine the mole numbers n'_R, n''_R, n'_W, n''_W for both states.
5. Assuming ideal mixtures for both phases, determine the volume change of the system.

22.8. Saturation Temperature and Pressure

1. Pure water at $p = 1$ bar boils at a temperature of 99.63 °C. How much salt must be added per kg of water to lower the saturation pressure for the same temperature by 1%?

2. For the same solution, find the boiling temperature for a pressure of 1.5 bar.

Note: NaCl dissociates in solution.

22.9. Water and Salt

A solution of salt (NaCl, $M_{\mathrm{NaCl}} = 58.5\frac{\mathrm{kg}}{\mathrm{kmol}}$) in water at 1.5 bar has a boiling temperature of 112 °C. How many grams of salt are dissolved in one litre of water?

Note: NaCl dissociates in solution.

22.10. Increase of Boiling Temperature

50 g sodium chloride are dissolved in 1 litre of water. Compute the boiling temperature at 1 bar.

22.11. Melting

In winter, after ice rain, a street is covered with a 1 cm thick layer of ice. What is the minimum mass of salt (NaCl) required per square meter to melt the ice when the temperature is $-10\,°\mathrm{C}$?

22.12. Cooling Liquid for a Car

The coolant of a car is required to freeze only below $-20\,°\mathrm{C}$. How many moles of ethylene glycol ($C_2H_6O_2$) or NaCl must be mixed to water, in order to lower the temperature of freezing to the required value? Why is glycol preferable above NaCl?

22.13. Cooking Pasta in the Mountains

A cylindrical pot (base area 250 cm^2, height 25 cm) contains 4 kg of pure water and 2 mol of NaCl. A lid which has a mass of 500 g rests freely on the top of the pot. The outside pressure is 0.8175 atm. At what temperature will the saltwater in the pot start to boil?

22.14. Boiling Point

100 g of glucose ($C_6H_{12}O_6$) and 20 g NaCl are dissolved in one litre of water, the mixture can be described as ideal mixture.

1. Find the boiling temperature of this mixture on a mountain, where the local pressure is 0.75 bar.
2. Determine the minimum work to remove only the salt, when the temperature is 23 °C.

22.15. A Lake

A lake in the mountains has a surface area of 1.2 km^2, its average depth is 24 m, and the water temperature is 17 °C. Air ($X_{N_2} = 0.79$, $X_{CO_2} = 0.0004$) at 0.8 bar stands over the water. Compute the masses of dissolved nitrogen and carbon dioxide.

22.16. Gas Mixture

Water is in contact with a gaseous mixture of nitrogen and carbon dioxide. The mole fractions of the gases in the liquid phase are measured as 1.1×10^{-4} for nitrogen and 0.006 for carbon dioxide. For a temperature of 25 °C, determine the mole fraction in the gas mixture, and the overall gas pressure.

22.17. Carbon Dioxide in Water

A piston cylinder system, which is maintained at a temperature of 298 K, contains 1 litre of liquid water, water vapor, and 5 g of carbon dioxide. The gas phase fills a volume of 1/10 litre.

1. Determine the pressure in the system.
2. Determine the percentage of CO_2 that is dissolved.

Hint: The solution becomes much easier with the assumption that in the liquid the mole amount of CO_2 is much smaller than the mole amount of water. If you use the assumption, verify it.

22.18. Henry's Law: Sparkling Water

A bottle of volume $V = 1.05$ litre contains 1 litre of liquid water, water vapor, and carbon dioxide. The pressure in the bottle is 2 bar at a temperature of 55 °C. Compute the masses of water and CO_2 in the bottle. Consider vapor and gaseous CO_2 as ideal gases. Ignore the volume (but not the amount) of dissolved CO_2 . Henry's law constant for CO_2: $H_{CO_2}(55\,°\mathrm{C}) = 3200\,\mathrm{bar}$.

22.19. Henry's Law: Nitrogen in Water I

A bottle of volume $V = 0.55$ litre contains 0.5 litre of liquid water, water vapor, and nitrogen. The pressure in the bottle is 1.5 bar at a temperature of 35 °C. Compute the masses of water and N_2 in the bottle. Consider vapor and gaseous N_2 as ideal gases. Ignore the volume of dissolved N_2. Henry's law constant for N_2: $H_{N_2}(35\,°\mathrm{C}) = 98600\,\mathrm{bar}$.

Remark: Guinness beer is nitrogenated with a special tab. This problem shows, why bottling it might give a very flat beer, unless a "widget" is used.

22.20. Henry's Law: Nitrogen in Water II

A bottle of total volume $V = 0.55$ litre contains 0.5 litre of liquid water, some water vapor, and a total of 0.006 mol of nitrogen. The temperature of the bottle and its contents is 35 °C.

1. Compute the total mass of water in the bottle (use tables).
2. Determine the amounts of nitrogen (in moles) dissolved in the liquid, and in the gas phase.
3. Determine the pressure in the bottle.

For the solution, ignore the volume (but not the amount) of dissolved N_2. Henry's law constant for N_2: $H_{N_2}\,(35\,°\mathrm{C}) = 98600\,\mathrm{bar}$.

22.21. A Diver

A deep sea diver breathes a mixture of 21% O_2 and 79% He, which is at the local water pressure. The divers body contains 5 litre of blood; for simplicity, assume that blood behaves like water.

1. Assume the blood (i.e., water at 36^oC) saturates with helium, and determine the amount (in moles) of helium dissolved in the blood at sea level and at a depth of 200 m.

2. For both cases determine also the volume (in litre) that the helium assumes at standard conditions.
3. Explain in thermodynamic terms why the driver needs to decompress slowly.

22.22. Henry's Law: Measurement of Oxygen Content of Lake Water

In order to retrieve water from deeper layers of a lake, the following simple device is suggested: A cylinder of volume $V = 0.11$ litre is filled with helium at 2 bar. The device is brought to the desired depth, and a valve is opened which allows water to enter the system, while the helium remains inside. Then the system is brought to the surface, and a sample of the water is taken to analyze the oxygen content.

The temperatures of all gases and liquids are assumed to be 9 °C, and the pressure on top of the lake is 0.9 bar. Density of water is 1 kg/litre. Henry's constant for O_2 in water at 9 °C is $H_{O_2}(T) = 31200\,\text{bar}$.

1. 100 ml of water enter the system—estimate the depth at which the valve was opened.
2. It is measured that the mole fraction of oxygen in the water sample is 1.1×10^{-6}. Use this information to compute the mole fraction of oxygen in the water where the sample was taken.

Hint: Obviously, some of the oxygen will gas out and enter the gas volume spanned by the helium, and this leads to a lower gas content in the liquid.

22.23. Measurement of Henry's Constant

To measure Henry's constant for oxygen in water, the following device is suggested. A container is divided into two equal parts, one part is filled with highly purified water, the other part is filled with oxygen at 10 bar. Then, the division is removed, and oxygen and water assume an equilibrium state. The gas pressure is measured as 9.66 bar, and throughout the measurement the temperature is kept at 20 °C. Determine Henry's constant $H_{O_2}(T)$, and the relative amount of oxygen that enters the liquid.

Hint: Ignore the change in volume due to oxygen entering the liquid.

22.24. Henry's Law: Mass of CO_2 In Air and Oceans

1. On earth, the pressure at ground level is 1 atm = 1.01325 bar, the gravitational acceleration is $9.81\frac{\text{m}}{\text{s}^2}$, and the earth radius is 6300 km. Use this data to compute the mass of the atmosphere.
2. 0.04 mole% of the air is carbon dioxide (CO_2) and 20.95 mole% is oxygen (O_2). Compute the masses of CO_2 and O_2 in the atmosphere.
3. 70% of the earth is covered by oceans and the average depth of the oceans is 4000 m. Assuming the mass density of the oceans is $1000\frac{\text{kg}}{\text{m}^3}$, compute the mass of water in the oceans.

4. For an average water temperature of 4 °C, compute the masses of CO_2 and O_2 dissolved in the worlds oceans. Use Henry's law in the form

$$X'_\alpha = \frac{p''_\alpha}{H_\alpha(T)} \, ,$$

where $H_\alpha(T)$ is Henry's law constant.

Comment: This problem assumes equilibrium conditions and ignores chemical effects. The actual amount of CO_2 dissolved differs from the value obtained here, due to formation of carbonic acid and carbonates, as well as non-equilibrium conditions.

22.25. Azeotropic Curves

Consider a binary mixture in liquid-vapour equilibrium, for two substances whose vapor pressures follow the Antoine law $\ln p = A - \frac{B}{C+T}$, where p is pressure in bar, and T is the temperature in Kelvin, with

	A	B/K	C/K
component 1	9.1	2000	-25
component 2	9.0	2100	-25

Assume that the vapor can be described as an ideal gas, while the activity coefficients in the liquid phase are given as

$$\gamma_\alpha = \exp\left[\varepsilon_0 \frac{T_0}{T}\left(1 - X'_\alpha\right)^2\right] \, ,$$

where ε_0 is a measure for the energy of interaction between particles of different type and $T_0 = 300\,\mathrm{K}$.

1. Set up the two equations for Raoult's law for this case.
2. By eliminating X''_1, find the equation for the saturated liquid line, $p\left(X'_\alpha, T\right)$.
3. It is not possible to find the saturated vapor line analytically. Find a parameter form of the saturated vapor line $\left\{p\left(X'_\alpha, T\right), X''_\alpha\left(X'_\alpha, T\right)\right\}$, where X'_α plays the role of the curve parameter.
4. Plot the two lines, and the partial pressures in the vapor in a p-X-diagram for $\varepsilon_0 = -2, 0, 2$ (and other values of your choice) for $T = 300\,\mathrm{K}$ (and other values of your choice). Discuss the curves, in particular the azeotropic point.
5. Construct the T-X-diagram, and plot it for $p = 20\,\mathrm{bar}$.
6. Discuss distillation/rectification for a mixture with an azeotropic point. Is it possible to completely separate such a mixture by distillation?