Chapter 18
Mixtures

18.1 Introduction

Many applications of thermodynamics involve not single substances but mixtures. The challenge is to track mixture composition, and to find the property data for the given composition. As long as mixture composition does not change, one can deal with mixtures the same way as with simple substances, including tabulating their properties; our treatment of air is the prime example of this.

Mixture composition can change through mixing or separation processes, through phase changes when the components have different vapor pressures, and through chemical reactions.

There is a vast array of applications for mixture theory, in particular in chemical engineering. Applications to be discussed include desalination of seawater, osmotic power plants, phase equilibrium and distillation processes, chemical equilibrium and NH_3 production, and combustion.

In this and the following chapters we shall provide the tools to properly describe and evaluate these processes. The present chapter introduces additional properties to account for mixture composition, and relations between properties of components and the mixture as a whole.

18.2 Mixture Composition

We consider mixtures of ν components, indicated by greek subscripts $\alpha = 1, 2, \ldots, \nu$. The present chapter deals with non-reacting mixtures, reacting mixtures will be discussed later.

Throughout the following we assume that all components have the same temperature T. The mixture is contained in the volume V, and the mixing state is homogeneous, so that each component is equally distributed in V.

The composition of the mixture can either be described through the masses m_α of the components contained in the volume V, or by their amount in

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molecule numbers N_α. Rather than tracking actual particle numbers, one uses the mole as a unit for counting particles, with the mole number defined as

$$n_\alpha = \frac{N_\alpha}{A} = \frac{m_\alpha}{M_\alpha} \ . \tag{18.1}$$

Here $A = 6.022 \times 10^{23} \frac{1}{\mathrm{mol}}$ is Avogadro's number, which defines the number of particles in one mole, and M_α is the molar mass, i.e., the mass of 1 mol of particles of type α.

The total mass m and the total mole number n of the mixture are obtained by summation over all components,

$$m = \sum_{\alpha=1}^{\nu} m_\alpha \quad , \quad n = \sum_{\alpha=1}^{\nu} n_\alpha = \sum_{\alpha=1}^{\nu} \frac{m_\alpha}{M_\alpha} = \frac{m}{M} \ . \tag{18.2}$$

The last equation defines the average molar mass M of the mixture.

Often we will not be interested in the absolute amounts of the components, but in the relative amounts. Mass fraction c_α (sometimes denoted as ”mass concentration”) and mole fraction X_α are defined as

$$c_\alpha = \frac{m_\alpha}{m} \quad , \quad X_\alpha = \frac{n_\alpha}{n} = \frac{N_\alpha}{N} \ ; \tag{18.3}$$

according to their definitions we have

$$\sum_{\alpha=1}^{\nu} X_\alpha = \sum_{\alpha=1}^{\nu} c_\alpha = 1 \ . \tag{18.4}$$

18.3 Example: Composition and Molar Mass of Air

The average molar mass of a mixture is given by

$$M = \frac{m}{n} = \frac{1}{n} \sum_{\alpha=1}^{\nu} m_\alpha = \frac{1}{n} \sum_{\alpha=1}^{\nu} M_\alpha n_\alpha = \sum_{\alpha=1}^{\nu} M_\alpha X_\alpha \ . \tag{18.5}$$

Air is a mixture of several gases, the main components and their mole fractions and molar masses are

$$\begin{array}{lll}
\text{nitrogen:} & X_{\mathrm{N}_2} = 0.7808 & , \ M_{\mathrm{N}_2} = 28.02 \frac{\mathrm{kg}}{\mathrm{kmol}} \ , \\
\text{oxygen:} & X_{\mathrm{O}_2} = 0.2095 & , \ M_{\mathrm{O}_2} = 32 \frac{\mathrm{kg}}{\mathrm{kmol}} \ , \\
\text{argon:} & X_{\mathrm{Ar}} = 0.0093 & , \ M_{\mathrm{Ar}} = 39.94 \frac{\mathrm{kg}}{\mathrm{kmol}} \ , \\
\text{carbon dioxide:} & X_{\mathrm{CO}_2} = 0.000397 & , \ M_{\mathrm{CO}_2} = 44.01 \frac{\mathrm{kg}}{\mathrm{kmol}} \ .
\end{array}$$

Accordingly, the average molar mass of air is $M_{\text{air}} = 28.97 \frac{\text{kg}}{\text{kmol}}$. The corresponding mass fractions are

$$c_\alpha = \frac{m_\alpha}{m} = \frac{n_\alpha M_\alpha}{nM} = X_\alpha \frac{M_\alpha}{M} \ ,$$

so that

$$c_{\text{N}_2} = 0.755,\ c_{\text{O}_2} = 0.231,\ c_{\text{Ar}} = 0.013,\ c_{\text{CO}_2} = 0.000455 \ .$$

18.4 Mixture Properties

In previous chapters, we have mainly used specific properties, that is properties per unit mass which are denoted as, e.g., $v_\alpha, u_\alpha, h_\alpha,\ s_\alpha$. For mixtures it is often more convenient do refer to particle numbers, and thus we will often use mole based properties, denoted as, e.g., $\bar{v}_\alpha, \bar{u}_\alpha, \bar{h}_\alpha,\ \bar{s}_\alpha$.

Mole and mass based quantities are related through the molar mass M_α, in particular we have

mass/mole density: $\rho_a = \frac{m_\alpha}{V} \ ,\ \bar{\rho}_a = \frac{n_\alpha}{V} \ ,$

specific/molar volume: $v_\alpha = \frac{V}{m_\alpha} \ ,\ \bar{v}_\alpha = \frac{V}{n_\alpha} = v_\alpha M_\alpha \ ,$

specific/molar internal energy: $u_\alpha \ ,\ \bar{u}_\alpha = u_\alpha M_\alpha \ ,$

specific/molar enthalpy: $h_\alpha \ ,\ \bar{h}_\alpha = h_\alpha M_\alpha \ ,$

specific/molar entropy: $s_\alpha \ ,\ \bar{s}_\alpha = s_\alpha M_\alpha \ .$

Properties of the mixture are obtained as weighted sums over the properties of the individual components. We study this for the total internal energy, for which we have

$$U = mu = \sum_{\alpha=1}^{\nu} m_\alpha u_\alpha = n\bar{u} = \sum_{\alpha=1}^{\nu} n_\alpha \bar{u}_\alpha \ . \tag{18.6}$$

The specific internal energy, and the molar internal energy of the mixture are obtained by division with m or n, as

$$u = \frac{U}{m} = \sum_{\alpha=1}^{\nu} c_\alpha u_\alpha \ \ ,\quad \bar{u} = \frac{U}{n} = \sum_{\alpha=1}^{\nu} X_\alpha \bar{u}_\alpha \ . \tag{18.7}$$

Enthalpy and entropy of the mixture are obtained in the same way:

$$h = \sum_{\alpha=1}^{\nu} c_\alpha h_\alpha \ \ ,\quad \bar{h} = \sum_{\alpha=1}^{\nu} X_\alpha \bar{h}_\alpha \ , \tag{18.8}$$

$$s = \sum_{\alpha=1}^{\nu} c_\alpha s_\alpha \ \ ,\quad \bar{s} = \sum_{\alpha=1}^{\nu} X_\alpha \bar{s}_\alpha \ . \tag{18.9}$$

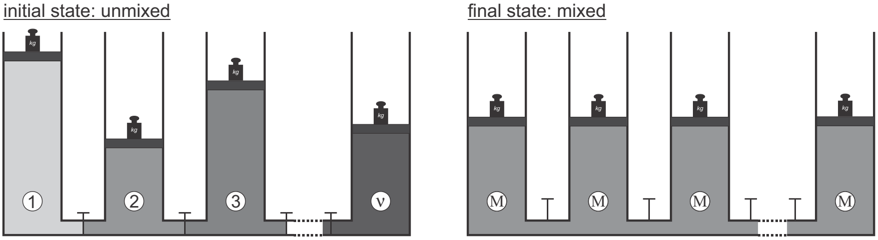

Fig. 18.1 Mixing of components at constant T and p

Above, we have not indicated the dependencies between properties. In general, the properties of one component will depend on the presence of all other components. For instance, the internal energy of component α will depend on temperature T and total pressure p of the mixture, and on all mole fractions X_β, $\beta = 1, \ldots, \nu$, that is $\bar{u}_\alpha = \bar{u}_\alpha(T, p, X_\beta)$. Therefore tabulated data for single components (where $X_\alpha = 1$ and $X_\beta = 0$ for $\beta \neq \alpha$) normally cannot be used. As will be seen, tabulated data for pure components can only be used for ideal gas mixtures, and ideal mixtures.

While all components have the same temperature T, they contribute to pressure differently. The partial pressure p_α is the contribution of component α to total pressure p, with

$$p = \sum_{\alpha=1}^{\nu} p_\alpha \ . \tag{18.10}$$

Note that, in general, $p_\alpha = p_\alpha(T, p, X_\beta)$, that is the partial pressure of a component will depend on the state and composition of the mixture.

18.5 Mixing Volume, Heat of Mixing and Entropy of Mixing

As components are mixed at constant temperature and pressure the extensive properties might change. To properly account for the change, we consider ν components in an initial unmixed state (I) where each component is at the same temperature, T, and pressure, p. The components are mixed while keeping temperature and pressure constant, the final state (E) is a homogeneous mixture, see Fig. 18.1. We ask for the corresponding changes in total volume, total enthalpy, and total entropy.

The volume change between initial and final state is computed as[1]

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[1] This and the other equations in this section are written with molar quantities and mole numbers. It is straightforward to write all in specific properties and masses, e.g. $V_{\text{mix}} = m_\gamma v_\gamma(T, p, c_\beta) - \sum_{\alpha=1}^{\nu} m_\alpha v_\alpha(T, p)$.

$$V_{\mathrm{mix}} = V_E - V_I = n_\gamma \bar{v}_\gamma \left(T, p, X_\beta\right) - \sum_{\alpha=1}^{\nu} n_\alpha \bar{v}_\alpha \left(T, p\right) \ , \tag{18.11}$$

where $\bar{v}_\alpha (T, p)$ denotes the specific volume of component α alone at (T, p) and $\bar{v}_\gamma (T, p, X_\beta)$ denotes the specific volume of *any* component γ in the mixture of composition X_β $(\beta = 1, \ldots, \nu)$ at (T, p). Note that in the mixed state all components are distributed over the volume of the mixture, V_E.

The change of volume is due to spatial hindrances or advantages on the molecular scale. For instance a mixture of 1 litre of water with 1 litre of ethanol (C_2H_5OH) yields a mixing volume of 1.93 litres.

When volume ratios are used to define the composition of a mixture, it must be clarified whether the volume of the component is related to the volume of the mixture, V_E, or the to the total volume of the components *before* mixing, V_I. A widely used measure for the alcohol content of beverages is "percent of alcohol by volume", defined as volume of the ethanol component *alone* over total volume of the *mixture*,

$$\%\mathrm{ABV} = \frac{m_{alc} v_{alc} \left(T, p\right)}{V_E} \ .$$

Isothermal mixing of components might release or require heat, which must be transferred. The first law applied to the isothermal and isobaric mixing process yields

$$H_{\mathrm{mix}} = H_E - H_I = \sum_{\alpha=1}^{\nu} n_\alpha \left[\bar{h}_\alpha \left(T, p, X_\beta\right) - \bar{h}_\alpha \left(T, p\right)\right] \ , \tag{18.12}$$

where H_{mix} is the heat that must be exchanged in order to keep the temperature T constant for the mixing process. Here, $\bar{h}_\alpha (T, p)$ is the molar enthalpy of component α alone at (T, p) and $\bar{h}_\alpha (T, p, X_\beta)$ is the molar enthalpy of the component α in a mixture of composition X_β $(\beta = 1, \ldots, \nu)$ at (T, p).

The enthalpy and internal energy are influenced by the interaction potential between molecules. In a pure substance, particles of type α interact only with particles of the same type. In a mixture, however, particles of type α are surrounded by different types of particles β $(\beta = 1, \ldots, \nu)$, which leads to different molecular interaction potentials, and thus a change in internal energy $\bar{u}_\alpha$ and enthalpy $\bar{h}_\alpha$ for the particles of type α as compared to the pure substance. A more detailed exploration of this will come in Sec. 22.9.

The entropy of mixing is computed in the same way, as

$$S_{\mathrm{mix}} = S_E - S_I = \sum_{\alpha=1}^{\nu} n_\alpha \left[\bar{s}_\alpha \left(T, p, X_\beta\right) - \bar{s}_\alpha \left(T, p\right)\right] \ . \tag{18.13}$$

We shall discuss the enthalpy and entropy of mixing as we proceed. To simplify the discussion we shall ignore volume changes from now on.

18.6 Ideal Gas Mixtures

We first consider ideal gas mixtures, which are particularly simple. In ideal gases, due to the large average distance between particles, the potential energies between particles can be ignored against their microscopic kinetic energies. Then, the individual components are not affected by the presence of other components, there is no enthalpy of mixing, and the ideal gas law holds for the individual components and the mixture.[2]

The partial pressure of one component distributed over the mixture volume V is given by the ideal gas law

$$p_\alpha = \frac{m_\alpha}{V} R_\alpha T = \frac{n_\alpha}{V} \bar{R} T \; , \tag{18.14}$$

where $\bar{R} = 8.314 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}}$ is the universal gas constant, and $R_\alpha = \bar{R}/M_\alpha$. The second form of the ideal gas law shows that the behavior of all ideal gases depends only on mole number, temperature and volume, but not on the type of gas.

The total pressure is just the sum of the partial pressures. For ideal gases, where the partial pressures are unaffected by the presence of other molecules, this is known as Dalton's law (John Dalton, 1766-1844),

$$p = \sum_{\alpha=1}^{\nu} p_\alpha = \sum_{\alpha=1}^{\nu} \frac{n_\alpha}{V} \bar{R} T = \frac{n}{V} \bar{R} T = \frac{m}{V} R T \; . \tag{18.15}$$

Here $R = \bar{R}/M$ is the gas constant for the mixture and M is the mixture's mean molar mass (18.5). Thus, with the proper molar masses, the components and the mixture obey the ideal gas law.

Division of the ideal gas laws for the component and the mixture shows that for ideal gas mixtures the pressure ratio equals the mole ratio,

$$\frac{p_\alpha}{p} = \frac{n_\alpha}{n} = X_\alpha \; . \tag{18.16}$$

In case that the ideal gas mixture is separated, so that each individual component is at the mixture pressure p and temperature T in its own volume V_α, the ideal gas law for the components reads

$$V_\alpha = \frac{n_\alpha \bar{R} T}{p} \quad \text{with} \quad \sum_{\alpha=1}^{\nu} V_\alpha = \sum_{\alpha=1}^{\nu} \frac{n_\alpha \bar{R} T}{p} = \frac{n \bar{R} T}{p} = V \; . \tag{18.17}$$

Here, V is the volume of the mixture in the mixed state. This is Amagat's law (Émile Amagat 1841-1915) which states that there will be no volume

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[2] Recall the van der Waals equation $p = \frac{RT}{v-b} - \frac{a}{v^2}$, where the second term accounts for attractive forces between the molecules; for large specifc volume $\frac{a}{v^2} \to 0$ and $v - b \to v$.

change when ideal gases are mixed, $V_{\text{mix}} = 0$, as long as the pressures and temperatures before and after mixing are the same.

18.7 Energy, Enthalpy and Specific Heats for Ideal Gases

For ideal gases, all energies and enthalpies depend only on the temperature T. The potential energy between particles is not relevant due to their large average distance, and thus there is no energy of mixing ($U_{\text{mix}} = 0$), and no enthalpy of mixing, $H_{\text{mix}} = U_{\text{mix}} + pV_{\text{mix}} = 0$. With that, the energies and enthalpies of the components have the same temperature dependence in the mixture and in the pure state,

$$u\left(T, c_\alpha\right) = \sum_{\alpha=1}^{\nu} c_\alpha u_\alpha\left(T\right) \quad , \quad \bar{u}\left(T, X_\alpha\right) = \sum_{\alpha=1}^{\nu} X_\alpha \bar{u}_\alpha\left(T\right) \ , \tag{18.18}$$

$$h\left(T, c_\alpha\right) = \sum_{\alpha=1}^{\nu} c_\alpha h_\alpha\left(T\right) \quad , \quad \bar{h}\left(T, X_\alpha\right) = \sum_{\alpha=1}^{\nu} X_\alpha \bar{h}_\alpha\left(T\right) \ . \tag{18.19}$$

Specific heats for the components and the mixture follow from differentiation with respect to temperature,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_{v,c_\beta} = \sum_{\alpha=1}^{\nu} c_\alpha c_{v,\alpha} \quad , \quad \bar{c}_v = \left(\frac{\partial \bar{u}}{\partial T}\right)_{v,X_\beta} = \sum_{\alpha=1}^{\nu} X_\alpha \bar{c}_{v,\alpha} , \tag{18.20}$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_{p,c_\beta} = \sum_{\alpha=1}^{\nu} c_\alpha c_{p,\alpha} \quad , \quad \bar{c}_p = \left(\frac{\partial \bar{h}}{\partial T}\right)_{p,X_\beta} = \sum_{\alpha=1}^{\nu} X_\alpha \bar{c}_{p,\alpha} . \tag{18.21}$$

Here, $c_{v,\alpha} = \frac{du_\alpha(T)}{dT}$ etc. are the specific heats for the pure components.

18.8 Entropy of Mixing for Ideal Gas

While volume, energy and enthalpy do not change when originally separated ideal gases at (T, p) (state I) are mixed, so that the mixture is at (T, p) (state II), the entropy does change. We compute the entropy for the two cases.

Component α fills the mixture volume V at temperature T and is at its partial pressure p_α. Its entropy is not affected by the presence of other components, it reads just as for a single component,

$$\bar{s}_\alpha\left(T, p_\alpha\right) = \bar{s}_\alpha^0\left(T\right) - \bar{R} \ln \frac{p_\alpha}{p_0} \ , \tag{18.22}$$

where $\bar{s}_\alpha^0\left(T\right)$ denotes the entropy of α alone at (T, p_0) and is tabulated.

With $X_\alpha = \frac{p_\alpha}{p}$ the molar entropy of one component in the mixture can be rewritten as

$$\bar{s}_\alpha \left(T, p, X_\beta\right) = \bar{s}^0_\alpha \left(T\right) - \bar{R} \ln X_\alpha - \bar{R} \ln \frac{p}{p_0} \; . \tag{18.23}$$

Accordingly, the entropy of component α depends only on the relative amount of α, while the composition of other components X_β $(\beta \neq \alpha)$ does not play a role.

In the unmixed state, all components are at (T, p) (i.e., $X_\alpha = 1$), and in the mixed state the components are at (T, p_α). The corresponding total entropies follow from summation over all components as

$$S_{\mathrm{I}} = \sum_{\alpha=1}^{\nu} n_\alpha \left[\bar{s}^0_\alpha \left(T\right) - \bar{R} \ln \frac{p}{p_0}\right] \; , \tag{18.24}$$

$$S_{\mathrm{II}} = \sum_{\alpha=1}^{\nu} n_\alpha \left[\bar{s}^0_\alpha \left(T\right) - \bar{R} \ln X_\alpha - \bar{R} \ln \frac{p}{p_0}\right] \; . \tag{18.25}$$

The entropy of mixing is just the difference,

$$S_{\mathrm{mix}} = S_{\mathrm{II}} - S_{\mathrm{I}} = -\bar{R} \sum_{\alpha=1}^{\nu} n_\alpha \ln \frac{p_\alpha}{p} = -\bar{R} \sum_{\alpha=1}^{\nu} n_\alpha \ln X_\alpha > 0 \; . \tag{18.26}$$

The entropy of mixing is positive, since $X_\alpha \leq 1$. Thus, entropy grows in mixing, and we conclude that mixing is an irreversible process, with a work loss. We shall later discuss how work could be obtained by reversible mixing.

The molar entropy of a mixture follows from (18.25) by division with the mole number n as

$$\bar{s} = \sum X_\alpha \bar{s}_\alpha \left(T, p, X_\beta\right) = \sum X_\alpha \left(\bar{s}^0_\alpha \left(T\right) - \bar{R} \ln X_\alpha - \bar{R} \ln \frac{p}{p_0}\right) \; . \tag{18.27}$$

18.9 Gibbs Paradox

We consider two different ideal gases in a container of Volume V, halved by a slider. Both gases are at the same temperature and pressure (T, p), and their mole numbers are equal $n_1 = n_2 = \frac{n}{2}$. When the slider is pulled out, the two gases mix while pressure and temperature remain unchanged. The partial pressures for both gases are

$$p_1 = p_2 = \frac{n_1 RT}{V} = \frac{n}{2} \frac{RT}{V} = \frac{p}{2} \; . \tag{18.28}$$

In the final equilibrium state, both gases are evenly distributed throughout the container. Entropy has grown, and the entropy of mixing for this process is

$$S_{\rm mix} = -\bar{R}\sum_{\alpha=1}^{2} n_\alpha \ln\frac{p_\alpha}{p} = n\bar{R}\ln 2 > 0\ . \tag{18.29}$$

When the slider is pushed back to separate the two parts of the container, the state is quite different from the initial state, since both parts now contain mixture. The difference between the two states becomes manifest in the positive value of the entropy of mixing.

Let us now consider that both gases are identical. The slider can be pulled out and pushed back at any time, without any change in the state of the gas, which is always the same gas at (T, p) in both compartments. Yet, the expression for the entropy of mixing, Eq. (18.29), predicts an entropy increase. This increase should not be present for a single gas, and thus the prediction of a positive entropy of mixing is considered to be a paradox, known as Gibbs paradox.

The paradox can be resolved by noting that the particles of just one type of gas cannot be distinguished. In particular, we cannot recognize whether an arbitrary particle picked from the gas was originally in a particular partition of the container. Indeed, could we mark the particles in one of the partitions at the initial time (before the slider is pulled out), the final state would show that particles that were on one side initially are now distributed over the whole container. In short, the entropy of mixing can only be computed for the mixing of distinguishable species.

18.10 Example: Isentropic Expansion through a Nozzle

We consider the isentropic expansion of a mixture of oxygen ($X_{\rm O_2} = 0.2$) and carbon dioxide ($X_{\rm CO_2} = 1 - X_{\rm O_2} = 0.8$) entering a nozzle at $\mathcal{V}_1 = 25\frac{\rm m}{\rm s}$, $p_1 = 6\,{\rm bar}$, $T_1 = 1200\,{\rm K}$ and leaving at $p_2 = 1\,{\rm bar}$. We ask for the temperature T_2 and the velocity $\mathcal{V}_2$ at the nozzle exit.

The molar mass of the mixture is $M = X_{\rm O_2} M_{\rm O_2} + X_{\rm CO_2} M_{\rm CO_2} = 41.6\frac{\rm kg}{\rm kmol}$. Since the process is reversible and adiabatic, it is isentropic, that is the molar entropy (18.27) of the mixture stays constant,

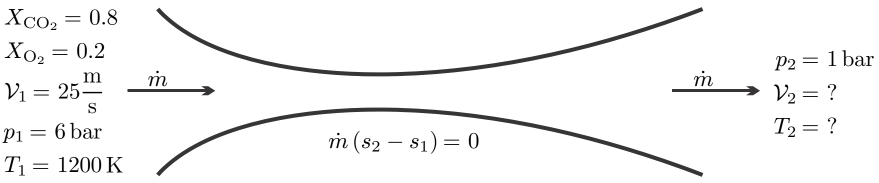

Fig. 18.2 Isentropic expansion in nozzle

$$\bar{s}_1 = \bar{s}_2 \ .$$

Since the mixing state does not change, this results in

$$\begin{aligned} X_{\mathrm{O}_2}\left[\bar{s}^0_{\mathrm{O}_2}\left(T_1\right) - \bar{R}\ln X_{\mathrm{O}_2} - \bar{R}\ln\frac{p_1}{p_0}\right] \\ + X_{\mathrm{CO}_2}\left[\bar{s}^0_{\mathrm{CO}_2}\left(T_1\right) - \bar{R}\ln X_{\mathrm{CO}_2} - \bar{R}\ln\frac{p_1}{p_0}\right] = \\ X_{\mathrm{O}_2}\left[\bar{s}^0_{\mathrm{O}_2}\left(T_2\right) - \bar{R}\ln X_{\mathrm{O}_2} - \bar{R}\ln\frac{p_2}{p_0}\right] \\ + X_{\mathrm{CO}_2}\left[\bar{s}^0_{\mathrm{CO}_2}\left(T_2\right) - \bar{R}\ln X_{\mathrm{CO}_2} - \bar{R}\ln\frac{p_2}{p_0}\right] \end{aligned}$$

or, after simplifying,

$$X_{\mathrm{O}_2}\bar{s}^0_{\mathrm{O}_2}\left(T_2\right) + X_{\mathrm{CO}_2}\bar{s}^0_{\mathrm{CO}_2}\left(T_2\right) = X_{\mathrm{O}_2}\bar{s}^0_{\mathrm{O}_2}\left(T_1\right) + X_{\mathrm{CO}_2}\bar{s}^0_{\mathrm{CO}_2}\left(T_1\right) + \bar{R}\ln\frac{p_2}{p_1} \ .$$

The right hand side can be computed from tabulated data as

$$A\left(T_2\right) = X_{\mathrm{O}_2}\bar{s}^0_{\mathrm{O}_2}\left(T_2\right) + X_{\mathrm{CO}_2}\bar{s}^0_{\mathrm{CO}_2}\left(T_2\right) = 259.20\frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \ .$$

The temperature T_2 must be found from trial and error, and interpolation. We find $A\left(890\,\mathrm{K}\right) = 258.90\frac{\mathrm{kJ}}{\mathrm{kmol\,K}}$ and $A\left(900\,\mathrm{K}\right) = 259.46\frac{\mathrm{kJ}}{\mathrm{kmol\,K}}$ and conclude from interpolation that $T_2 = 895.4\,\mathrm{K}$.

The velocity follows from the first law for the nozzle as

$$\mathcal{V}_2 = \sqrt{2\left(h_1 - h_2\right) + \mathcal{V}_1^2} \ .$$

We have

$$h_1 - h_2 = \frac{1}{M}\left[X_{\mathrm{O}_2}\left(\bar{h}_{\mathrm{O}_2}\left(T_1\right) - \bar{h}_{\mathrm{O}_2}\left(T_2\right)\right) + X_{\mathrm{CO}_2}\left(\bar{h}_{\mathrm{CO}_2}\left(T_1\right) - \bar{h}_{\mathrm{CO}_2}\left(T_2\right)\right)\right] \ ,$$

and thus $h_1 - h_2 = 372.7\frac{\mathrm{kJ}}{\mathrm{kg}}$ and $\mathcal{V}_2 = 611\frac{\mathrm{m}}{\mathrm{s}}$.

18.11 Example: Isochoric Mixing of Two Gases at Different *p*, *T*

We consider an adiabatic rigid container of volume V which is separated by a membrane. The two parts of the container hold different ideal gases, with the given data $\left(m_1, T_1^I, p_1^I, M_1, c_{v,1}\right)$ and $\left(m_2, T_2^I, p_2^I, M_2, c_{v,2}\right)$, the superscript I indicates the initial state, the final state will be denoted with superscript E. To simplify the problem we assume the specific heats to be constant.

The dividing membrane is removed, and we ask for the final pressure and temperature, and for the amount of entropy generated.

The volumes of the compartments and of the container are

$$V_1 = \frac{n_1 \bar{R} T_1^I}{p_1^I} \quad , \quad V_2 = \frac{n_2 \bar{R} T_2^I}{p_2^I} \quad , \quad V = V_1 + V_2 \; .$$

Since the container is adiabatic and rigid, $V = const.$, the first law applied to the volume V gives that the total internal energy is constant, $U^I = U^E$, so that the final temperature is

$$T^E = \frac{m_1 c_{v,1} T_1^I + m_2 c_{v,2} T_2^I}{m_1 c_{v,1} + m_2 c_{v,2}} = \frac{X_1 \bar{c}_{v,1} T_1^I + X_2 \bar{c}_{v,2} T_2^I}{X_1 \bar{c}_{v,1} + X_2 \bar{c}_{v,2}} \; .$$

The final pressure follows from the ideal gas law for the mixture as

$$p^E = \frac{n \bar{R} T^E}{V} = \frac{1}{\frac{X_1 T_1^I}{p_1^I T^E} + \frac{X_2 T_2^I}{p_2^I T^E}} \; .$$

The change in entropy of the two gases is

$$\mathit{\Delta} S = n_1 \left[\bar{c}_{p,1} \ln \frac{T^E}{T_1^I} - \bar{R} \ln \frac{X_1 p^E}{p_1^I} \right] + n_2 \left[\bar{c}_{p,2} \ln \frac{T^E}{T_2^I} - \bar{R} \ln \frac{X_2 p^E}{p_2^I} \right] \; ,$$

which can be split into three contributions that refer to the entropy change due to heat exchange, pressure equilibration and mixing,

$$\begin{aligned} \mathit{\Delta} S = n & \left[X_1 \bar{c}_{p,1} \ln \frac{T^E}{T_1^I} + X_2 \bar{c}_{p,2} \ln \frac{T^E}{T_2^I} \right] \\ & + n\bar{R} \left[X_1 \ln \frac{p_1^I}{p^E} + X_2 \ln \frac{p_2^I}{p^E} \right] - n\bar{R} \left[X_1 \ln X_1 + X_2 \ln X_2 \right] \; . \end{aligned}$$

18.12 Ideal Mixtures

Ideal mixtures are defined as mixtures with vanishing volume and heat of mixing, and an entropy of mixing just as that of the ideal gas, i.e.,

$$V_{\mathrm{mix}} = H_{\mathrm{mix}} = 0 \quad , \quad S_{\mathrm{mix}} = -\sum_\alpha n_\alpha \bar{R} \ln X_\alpha \; . \tag{18.30}$$

Ideal gas mixtures are a special case of ideal mixtures. In particular, the theory of ideal mixtures can be applied to dilute liquid solutions.

As for the ideal gas, the first two conditions $(18.30)_{1,2}$ for ideal mixtures state that mixing does not affect energy. This would be the case if intermolecular potential of the various components are equal, or at least rather similar, so that the potential energy of a pair of identical molecules (α-α-pair) is similar to that of a dissimilar pair (α-β-pair).

The entropy of mixing warrants more detailed discussion. It is best motivated through Boltzmann's microscopic interpretation of entropy as discussed earlier, in Sec. 4.14. The microscopic definition of entropy reads

$$S = k \ln \Omega \,, \tag{18.31}$$

where $k = \bar{R}/A = 1.3806 \times 10^{-23} \frac{\mathrm{J}}{\mathrm{K}}$ is Boltzmann's constant, and Ω is the number of microscopic realizations of a given macroscopic state. For instance, for an ideal gas, simply speaking, a macroscopic state is given by the values of temperature, pressure, and velocity of the gas, while a microscopic state is given by the location and velocities of the gas particles. The entropy can be computed from (18.31) for rather complex systems, e.g., polymers, but for many systems the evaluation of the equation becomes too cumbersome to be done analytically.

A macroscopic state is for instance given by mass, volume, and temperature of a sample of substance. While the macroscopic state is maintained, due to the thermal motion of the particles the system runs through a succession of its accessible microscopic states. At standard condition, the average speed of a gas molecule is of the order of the speed of sound ($\sim 350 \frac{\mathrm{m}}{\mathrm{s}}$), and it undergoes about 10^{10} collisions per second. Accordingly, the system goes through a vast number of microstates per second.

While the full evaluation of $S = k \ln \Omega$ requires consideration of the full microstate, i.e., locations and velocities of particles, we can consider the locations alone to compute the entropy of mixing. We study a container with $N = \sum_\alpha N_\alpha$ particles of different types $\alpha = 1, \ldots, \nu$. We divide the container into N cells of equal size, and assume that there can be only one particle per cell. Since we cannot distinguish between different particles of the same kind, the number of possibilities to distribute the $\sum_\alpha N_\alpha$ particles over the N cells is

$$\Omega = \frac{N!}{\prod N_\alpha!} \,. \tag{18.32}$$

The corresponding macrostate for a mixed state is simply to have $N = \sum_\alpha N_\alpha$ particles in the container.

Before we further evaluate this expression, we study the example of just four particles of two different types, two of each type. In the state before mixing, a wall separates the different components into the configuration $\big[1\ 1 \,||\, 2\ 2\big]$. There is only one microscopic realization of this configuration, since the particles cannot pass the wall. As soon as the wall is removed, the particles can exchange positions due to thermal motion, and thus access a larger number of microstates. Equation (18.32) gives $\Omega = 6$; the states are

$$\begin{bmatrix} 1 & 1 & 2 & 2 \\ 2 & 2 & 1 & 1 \\ 1 & 2 & 1 & 2 \\ 2 & 1 & 1 & 2 \\ 1 & 2 & 2 & 1 \\ 2 & 1 & 2 & 1 \end{bmatrix} .$$

Thus, the mixed state, where the wall is removed has more microscopic realizations than the unmixed state, and the higher entropy.

Note that the original configuration forms one of the accessible microstates of the unrestrained system as well. The probability that this state is $1/\Omega$, which is indeed the probability that *any* particular microstate is assumed. For real systems, the particle numbers are huge, and the number of possible configurations is enormous. The probability to find the original configuration, which was maintained by the wall before it was removed, is negligible, and most microstates will be mixed—thus mixed states will be observed.

We proceed to evaluate (18.31) with (18.32) for large numbers N_α. By means of Stirling's formula $\ln N! \simeq N \ln N - N$, which holds for large N, we find

$$\begin{aligned} S_{\text{mix}} = k \ln \frac{N!}{\prod N_\alpha!} &= k \left(N \ln N - \sum_\alpha N_\alpha \ln N_\alpha \right) \\ &= k \sum_\alpha \left(N_\alpha \ln N - N_\alpha \ln N_\alpha \right) . \end{aligned} \tag{18.33}$$

When we introduce the mole number $n_\alpha = N_\alpha / A$, the mole fraction $X_\alpha = \frac{n_\alpha}{n} = \frac{N_\alpha}{N}$, and $\bar{R} = kA$, we recover $(18.30)_3$,

$$S_{\text{mix}} = - \sum_\alpha n_\alpha \bar{R} \ln X_\alpha . \tag{18.34}$$

In thermodynamic systems the number of particles is normally very large, with 6.022×10^{23} particles per mole. For example in an equimolar binary mixture with $N_1 = N_2 = 10^{23}$ one finds $\ln \Omega = 1.386 \times 10^{23}$, $S_{\text{mix}} = 1.9139 \frac{\text{J}}{\text{K}}$. The probability to recover the initial unmixed state as one of the microstates is incredibly small at $\frac{1}{\Omega} = 4^{-10^{23}}$: spontaneous unmixing is not impossible, but incredibly unlikely, and cannot be expected to be observed in the lifetime of the universe. Return to Sec. 4.14 for additional discussion on the microscopic interpretation of entropy.

The computation of the entropy of mixing in this section relied on the assumption that there are as many location cells as particles, which is appropriate for simple liquids. The reader might wonder how the entropy of mixing for an ideal gas comes about, for which there are far more cells than particles. We briefly run through the necessary arguments: To deal with an ideal gas mixture, we consider empty cells as an additional species with count

N_e. With $N = N_g + N_e$ as the total number of cells and $N_g = \sum_\alpha N_\alpha$ as number of gas particles, we have one additional term:

$$\begin{aligned} S_{\text{mix,id.gas}} &= k \ln \frac{N!}{N_e! \prod N_\alpha!} \\ &= k \left[\sum_\alpha \left(N_\alpha \ln N - N_\alpha \ln N_\alpha \right) + \left(N_e \ln N - N_e \ln N_e \right) \right] \end{aligned} \quad (18.35)$$

With the mole fraction of gas species $X_\alpha = N_\alpha / N$, this can be simplified to

$$S_{\text{mix,id.gas}} = -k \sum_\alpha N_\alpha \ln X_\alpha + k N_g \left[\ln \frac{N}{N_g} - \frac{N - N_g}{N_g} \ln \frac{N - N_g}{N} \right] . \quad (18.36)$$

The first term is the entropy of mixing as discussed before. We proceed with the discussion of the second term. The total volume filled by the gas is $V = N v_c$, where v_c is the cell volume. Therefore $\ln \frac{N}{N_g} = \ln \frac{\bar{v}}{\bar{v}_0}$, where $\bar{v}$ is mole volume and $\bar{v}_0 = v_c A$ is a reference mole volume. For the ideal gas, there are far more cells than gas particles, so that $N \gg N_g$, and in the limit we find $\lim_{\frac{N_g}{N} \to 0} \frac{N - N_g}{N_g} \ln \frac{N - N_g}{N} = -1$. Hence, with $k = \bar{R}/A$, we find three contributions to ideal gas entropy, namely entropy of mixing, the well-known volume dependence of entropy, and a constant,

$$S_{\text{id.gas}} = \bar{R} n_g \left[-\sum_\alpha X_\alpha \ln X_\alpha + \ln \frac{\bar{v}}{\bar{v}_0} + 1 \right] . \quad (18.37)$$

18.13 Entropy of Mixing and Separation Work

We consider mixing and separation of ideal mixtures at constant temperature T. The combined first and second law for a closed system at constant temperature T reads

$$\dot{W} = -T \dot{S}_{gen} - \frac{dU - TS}{dt} , \quad (18.38)$$

or, after integration over the duration of the process,

$$W_{12} + T S_{gen} = -\left(U_2 - U_1 \right) + T \left(S_2 - S_1 \right) , \quad (18.39)$$

where $S_{gen} = \int_{t_1}^{t_2} \dot{S}_{gen} dt$ is the total entropy generation for the process.

We consider mixing first, where state 1 is the unmixed state, and state 2 is the mixed state. Then, since $U_{\text{mix}} = 0$ for an ideal mixture,

$$W_{12} + T S_{gen} = T S_{\text{mix}} - U_{\text{mix}} = T S_{\text{mix}} > 0 . \quad (18.40)$$

When the mixing is fully irreversible, no work is drawn, $W_{12} = 0$, and the entropy generation is just the entropy of mixing, $S_{gen} = S_{\text{mix}}$. However, the equation shows that it is possible to generate the work

$$W_{12} = TS_{\text{mix}} - TS_{gen} > 0 \ . \tag{18.41}$$

In a real device, the irreversibilities of the process diminish the work by TS_{gen}. The maximum work is obtained from a fully reversible process as

$$W_{\text{mix}}^{rev} = TS_{\text{mix}} \ . \tag{18.42}$$

Note that more work can be produced at higher temperature.

Now we consider separation, where state 1 is the mixed state, and state 2 is the unmixed state. Then, again with $U_{\text{mix}} = 0$,

$$W_{12} = -TS_{gen} - TS_{\text{mix}} < 0 \ . \tag{18.43}$$

Work is required for separation ($TS_{\text{mix}} > 0$) and to overcome irreversibilities in the device ($TS_{gen} > 0$). The minimum separation work is obtained or a fully reversible process, where $S_{gen} = 0$, as

$$W_{\text{sep}}^{rev} = -TS_{\text{mix}} \ . \tag{18.44}$$

The separation work is directly proportional to the entropy of mixing, less work is required for separation at lower temperatures.

Section 21 will present a closer look at desalination plants, which separate salt from water, and osmotic power plants, which use mixing for power generation. 21.5.

18.14 Non-ideal Mixtures

The equilibrium condition for a mixture at given pressure p and temperature T is that the Gibbs free energy assumes a minimum. We denote the Gibbs free energies of the unmixed and the mixed states by G_{unmixed}, G_{mixed}, respectively. Both are related as

$$G_{\text{mixed}} = G_{\text{unmixed}} + G_{\text{mix}} \ \text{ with } \ G_{\text{mix}} = H_{\text{mix}} - TS_{\text{mix}} \ . \tag{18.45}$$

The equilibrium state will be the mixed state for negative Gibbs free energy of mixing, $G_{\text{mix}} < 0$, so that $G_{\text{mixed}} < G_{\text{unmixed}}$, but it will be the unmixed state, if $G_{\text{mix}} > 0$, so that $G_{\text{unmixed}} < G_{\text{mixed}}$.

For an ideal mixture we have $H_{\text{mix}} = 0$, hence $G_{\text{mix}} = -TS_{\text{mix}} < 0$. Accordingly, ideal mixtures will assume a mixed equilibrium state.

The Gibbs free energy of mixing will only be positive if the enthalpy of mixing is large, that is for $H_{\text{mix}} > TS_{\text{mix}}$. Large enthalpy of mixing is observed when the intermolecular forces between like particles are much larger than those between unlike particles.

Due to its dipole structure, water has strong polar bonds between its molecules, while oil is non-polar. Breaking up the water bonds to form water-oil pairs instead of water-water pairs requires energy, and hence the enthalpy of mixing, H_{mix}, is positive. From the fact that oil separates from water, we can conclude that the energetic effect exceeds the entropic effect, that is $H_{\text{mix}} > TS_{\text{mix}}$.

Table salt (sodium chloride, NaCl) dissociates in water into charged ions, Na^+ and Cl^-, which have energetic bonds with water. Nevertheless, for water-salt solutions, the enthalpy of mixing is positive, but smaller than the entropic term TS_{mix}. In dilute solutions, the energetic interaction between salt ions and water molecules can be ignored, and the solution can be approximated as an ideal mixture. Dissociation requires shielding of salt ions by the polar water molecules, where several water molecules are shielding one salt ion. If all water molecules are used for the hydrogen shells, no additional salt ions can be dissolved, the solution becomes saturated.

Problems

18.1. Mixture Properties

An ideal gas mixture consists of 6 kg of O_2, 5 kg of N_2 and 12 kg of CO_2.

1. Determine the mass and mole fraction of each component.
2. Determine the average molar mass and the gas constant of the mixture.
3. Compute the partial pressures of all components when the total pressure is 2 bar.
4. Compute the entropy of mixing between mixed and unmixed state.

18.2. Heating of Mixture

A piston-cylinder device contains a mixture of 1 kg of H_2 and 2 kg of N_2, initially at 200 kPa and 280 K. The mixture is heated at constant pressure until the volume is three times the initial volume. Determine the temperature of the final state, the total heat transferred, and the change of entropy of the mixture. Use tabulated property data.

18.3. Isobaric Cooling of Mixture

A piston-cylinder device contains a mixture of 0.75 kg of N_2 and 2 kg of CO at 300 kPa and 860 K. Heat is now transferred from the mixture at constant pressure until the volume is one third of the initial volume. Determine the heat transfer, the work done, and the change of entropy. Use tabulated property data.

18.4. Mixing of H_2 and CO_2

An adiabatic rigid tank is divided into two parts. One part contains 4.4 kg of CO_2 at 25 °C and 200 kPa, and the other part contains 1 kg of H_2 at 80 °C and 400 kPa. After the divider is removed, the gases mix and the mixture assume a final equilibrium state.

1. Determine the equilibrium temperature and the equilibrium pressure.
2. Compute the entropy generated in the process.

Assume constant specific heats at 300 K for both gases.

18.5. Compressor

A compressor draws an ideal gas mixture (molar composition 50% CO_2, 33.3% CO, 16.7% O_2) at 37 °C, 1 bar, $50\frac{\mathrm{m}}{\mathrm{s}}$. The mass flow rate is $5\frac{\mathrm{kg}}{\mathrm{s}}$, and the exit state is 237 °C, $80\frac{\mathrm{m}}{\mathrm{s}}$. The compressor is not adiabatic, heat is lost to the surroundings at a rate of $3\frac{\mathrm{kJ}}{\mathrm{kg}}$ of mixture flowing.

1. Determine the power to run the compressor.
2. Assume that the compression is polytropic, and determine the polytropic exponent. Then find the exit pressure.

18.6. Adiabatic Turbine

The combustion product in a gas turbine system consists of nitrogen, oxygen, carbon dioxide and water with the following mole flow rates: $\dot{n}_{N_2} = 1.7\frac{\mathrm{kmol}}{\mathrm{s}}$, $\dot{n}_{O_2} = 0.15\frac{\mathrm{kmol}}{\mathrm{s}}$, $\dot{n}_{H_2O} = 0.25\frac{\mathrm{kmol}}{\mathrm{s}}$, $\dot{n}_{CO_2} = 0.2\frac{\mathrm{kmol}}{\mathrm{s}}$.

At turbine inlet, the pressure is 12 bar, and the temperature is 1500 K. Determine the power production of the turbine in isentropic expansion to an external pressure of 1 bar.

Hint: To estimate exit temperature for trial and error, you might want to look at expansion of air first.

18.7. Mixing and Separation

1 kg of argon at 10 bar, 400 K and 0.5 kg of xenon at 10 bar, 1000 K are isobarically and adiabatically mixed in a closed piston-cylinder system.

1. Determine the equilibrium temperature of the mixture.
2. Determine the initial system volume, and the volume change between initial and final state. Explain the result.
3. Find the reversible work required for separation of the mixture.

Remark: Both gases are monatomic, with $M_{\mathrm{Ar}} = 39.95\frac{\mathrm{kg}}{\mathrm{kmol}}$, and $M_{\mathrm{Xe}} = 131.3\frac{\mathrm{kg}}{\mathrm{kmol}}$.

18.8. Mixing of Argon and Helium

An adiabatic cylinder is closed by a moveable piston. The cylinder contains 4litres of argon at 150 kPa and a rubber balloon which contains 1litre of helium at 3 bar. Both gases are initially at a temperature of 25 °C, and the piston rests due to its own weight. Assume that the pressure volume characteristic of the balloon is of the form $\Delta p = a\left(V_B - V_0\right)^2$ where Δp is the pressure difference between inside and outside, V_B is the actual volume, the reference volume V_0 is 0.25litres, and a is a material constant. This implies that the balloon shell stores some energy when stretched. As soon as the balloon has reached the volume V_0, there are no further stresses in the balloon, and the balloon shell will just collapse. For simplicity, ignore the thermal mass of the balloon.

A small hole opens in the balloon through which all helium escapes; in the final equilibrium state the gases are mixed.

1. Determine the pressure, temperature and cylinder volume in the final equilibrium state.
2. Compute the entropy changes for both gases, and the total entropy generated in the process. Compare to the entropy of mixing, S_{mix}, and discuss the difference.