5.2 Caloric properties of ideal-gas mixtures

To calculate the chemical potential μ_i of one component i we combine Eq. (3.78) and $\mu = \Delta G_m$

$$\mu_i = \mu_i^0 + RT\ln\frac{p_i}{p^0} \quad \text{with} \quad p_i = x_i\, p_{tot} \quad \Rightarrow \quad \mu_i = \mu_i^0 + RT\ln x_i + RT\ln\frac{p_{tot}}{p^0} \tag{5.1}$$

This is Dalton's law. Normally p_{tot} and p^0 (the standard pressure) are selected 1 bar, thus, the second ln-term is vanishing.
For an extensive property Φ the difference by mixing compared to the pure components is

$$\Delta_{mix}\Phi^{id} = \Phi^{id}(mixture) - \sum_i n_i \Phi_m^{id}(pure) \tag{5.2}$$

Since no interaction between the ideal gas molecules exist we find

$$\Delta_{mix}H^{id} = \Delta_{mix}V^{id} = 0 \tag{5.3}$$

To calculate the effect of mixing on the entropy we apply the scheme of Fig. 5.1. Since S is a state function we can replace the calculation of mixing by expansion performed separately for each component. Since this ideal mixing is isothermal ($0 = dU = T\,dS - p\,dV$)

$$dS = \frac{p}{T}dV = \frac{n\,RT}{VT}dV = n\,R\,d\ln V \tag{5.4}$$

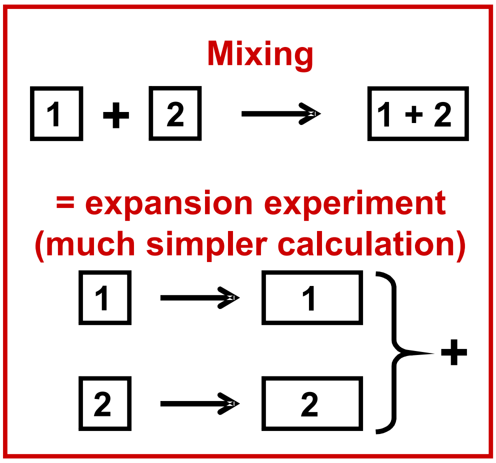

Figure 5.1: Scheme for mixing of two ideal gases.

so

$$\begin{aligned} &\Delta_{mix}S_1^{id} = n_1\,R\ln\frac{V_1+V_2}{V_1}, \qquad \Delta_{mix}S_2^{id} = n_2\,R\ln\frac{V_1+V_2}{V_2} \\ \Rightarrow\ &\Delta_{mix}S_1^{id} = -n_1\,R\ln x_1, \qquad \Delta_{mix}S_2^{id} = -n_2\,R\ln x_2 \\ \Rightarrow\ &\Delta_{mix}S^{id} = \Delta_{mix}S_1^{id} + \Delta_{mix}S_2^{id} = -\sum_i n_i\,R\ln x_i \end{aligned} \tag{5.5}$$

Thus

$$\Delta_{mix}G^{id} = \sum_i n_i\,RT\ln x_i \quad \text{i.e.} \quad \Delta_{mix}G_m^{id} = -T\,\Delta_{mix}S_m^{id} = \sum_i x_i\,RT\ln x_i \tag{5.6}$$

Since $\Delta_{mix}S > 0$ and $\Delta_{mix}G < 0$ mixing of gases is SPONTANEOUS, i.e. an irreversible process, even for ideal gases for which no energy contributions exist.