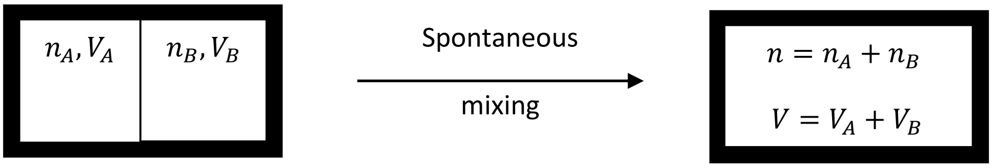
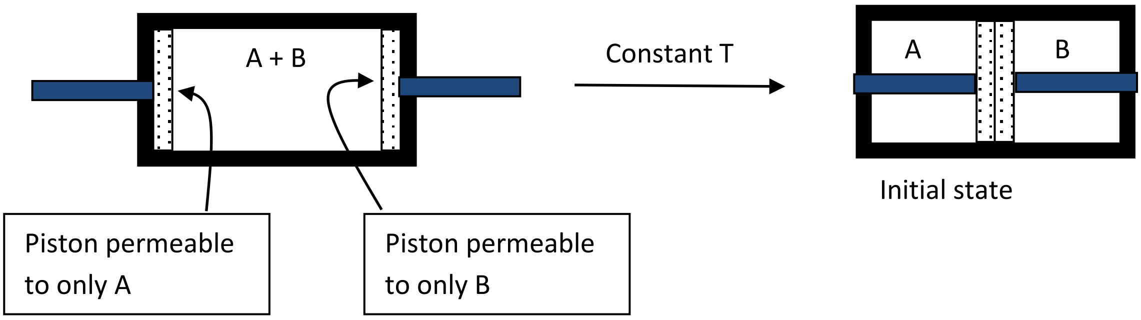
Mixing of an I.G. at constant T and p



$$n_A A(g, V, T) + n_B B(g, V, T) \rightarrow n_{A+B}(A+B)(g, V, T)$$

To find ΔS_{mixing} → find a reversible path

Demixing?



$$\Delta S_{demixing} = -\Delta S_{mixing}$$

For the reverse process, $\Delta U = 0 \quad \Rightarrow \quad q_{rev} = -w_{rev} = p_A dV_A + p_B dV_B$ (compression of each)

$$\Delta S_{demixing} = \int \frac{dq_{rev}}{T} = \int_V^{V_A} \frac{p_A dV_A}{T} + \int_V^{V_B} \frac{p_B dV_B}{T} = n_A R \ln \frac{V_A}{V} + n_B R \ln \frac{V_B}{V}$$

In terms of mole fractions, $X_i = \frac{n_i}{n}$ and $X_i = \frac{V_i}{V}$

$$\Delta S_{demixing} = nR[X_A \ln X_A + X_B \ln X_B]$$

Since $X_i < 1, \Delta S_{demixing} < 0, \; \Delta S_{mixing} > 0$ (mixed state is more disordered)

Irreversible phase change at constant T and p

e.g. $\mathrm{H_2O}\ (l, -10\ °\mathrm{C}, 1\ \mathrm{bar}) \rightarrow \mathrm{H_2O}\ (s, -10\ °\mathrm{C}, 1\ \mathrm{bar})$ --- spontaneous and irreversible

Find a reversible path.

Take water to $\mathrm{H_2O}\ (l,\ 0\ °\mathrm{C}, 1\ \mathrm{bar})$ by heating reversibly, $dq_{rev} = C_{p,l} dT$

Convert to $\mathrm{H_2O}\ (s,\ 0\ °\mathrm{C}, 1\ \mathrm{bar})$ reversible phase transformation $q_{rev} = -\Delta H_{fus}$

Cool down to $\mathrm{H_2O}\ (s, -10\ °\mathrm{C}, 1\ \mathrm{bar})$ reversible cooling, $dq_{rev} = C_{p,s} dT$

Measurement of Entropy

$$S(T) = S(0) + \int_0^{T_f} \frac{C_{p,s}dT}{T} + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,l}dT}{T} + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_{p,g}dT}{T}$$

The Third Law

Nernst Heat Theorem: The entropy changes accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \to 0$ as $T \to 0$ provided all the substances involved are perfectly crystalline.

The entropy of all perfect crystalline substances is zero at $T = 0$.