Entropy of mixing [tln25]

Consider two dilute gases in a rigid and insulating box separated by a mobile conducting wall: $n_1 = x_1 n$ (helium) and $n_2 = x_2 n$ (neon) with $x_1 + x_2 = 1$. Thermal equilibrium: p, T, $V_1 = x_1 V$, $V_2 = x_2 V$.

p T	p T
n_1 V_1	n_2 V_2

When the interior wall is removed, the gases mix spontaneously (irreversible process). By how much does the entropy increase?

To calculate ΔS, consider a reversible mixing process involving an isothermal expansion of semipermeable walls:

$$U = U_1 + U_2 \text{ with } U_i(T) = \text{const} \Rightarrow dU_i = TdS_i - p_i dV_i = 0.$$

$p_i = \dfrac{n_i RT}{V_i}$ are the partial pressures exerted on the semipermeable walls.

$$\Rightarrow dS_i = \frac{p_i}{T} dV_i = \frac{n_i R}{V_i} dV_i = nRx_i \frac{dV_i}{V_i}.$$

Entropy of mixing: $\Delta S = nR \sum_i x_i \int_{x_i V}^{V} \dfrac{dV_i}{V_i} = -nR \sum_i x_i \ln x_i > 0.$

Gibbs paradox: No entropy increase should result if the two gases happen to be of the same kind. This distinction is not reflected in the above derivation. The paradox is resolved by quantum mechanics, which requires that distinguishable and indistinguishable particles are counted differently.

To calculate the change in Gibbs free energy during mixing, we use the result for $G(T, p, N)$ of an ideal gas (see [tex15]) rewritten as $G(T, p, n) = -nRT \left[\ln(T/T_0)^{\alpha+1} - \ln(p/p_0) \right]$.

Initially: $p_1 = p_2 = p \Rightarrow G_{ini} = -\sum_i nx_i RT \left[\ln \left(\dfrac{T}{T_0} \right)^{\alpha+1} - \ln \dfrac{p}{p_0} \right].$

Finally: $p_i = px_i \Rightarrow G_{fin} = -\sum_i nx_i RT \left[\ln \left(\dfrac{T}{T_0} \right)^{\alpha+1} - \ln \dfrac{px_i}{p_0} \right].$

Change in Gibbs free energy: $\Delta G = nRT \sum_i x_i \ln x_i.$

Use $S = -\left(\dfrac{\partial G}{\partial T} \right)_p$ to recover $\Delta S = -nR \sum_i x_i \ln x_i.$

Change in chemical potential: use $G = \sum_i n_i \mu_i \Rightarrow \Delta \mu_i = RT \ln x_i.$