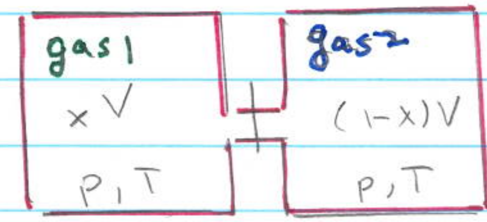
Entropy of Mixing

- Consider two gasses separated by a partition as shown below (see slide)



- The two gasses intermingle, when the valve is opened and entropy increases. Since the ΔS does not depend on the path we can replace the non-equilibrium process with an equilibrium one. We will connect the state A (gas with volume xV) to the final state B (gas with volume V) via an isothermal expansion

$$dS = \cancel{\frac{1}{T} dU}^{\,0} + \frac{p}{T} dV$$

- dU is zero since for an ideal gas, U is only a function of temperature

$$\Delta S_1 = \int_{xV_f}^{V_f} \underbrace{\left(\frac{N_1 k T}{V\,T}\right)}_{\text{this is } \frac{p}{T}} dV = N_1 k \log\left(\frac{V_f}{x V_f}\right) = -N_1 k \log x$$

Entropy of Mixing

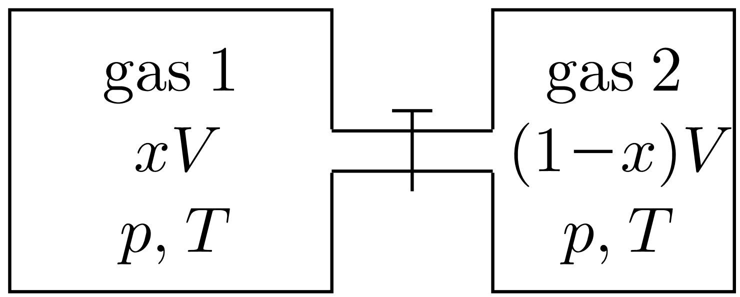
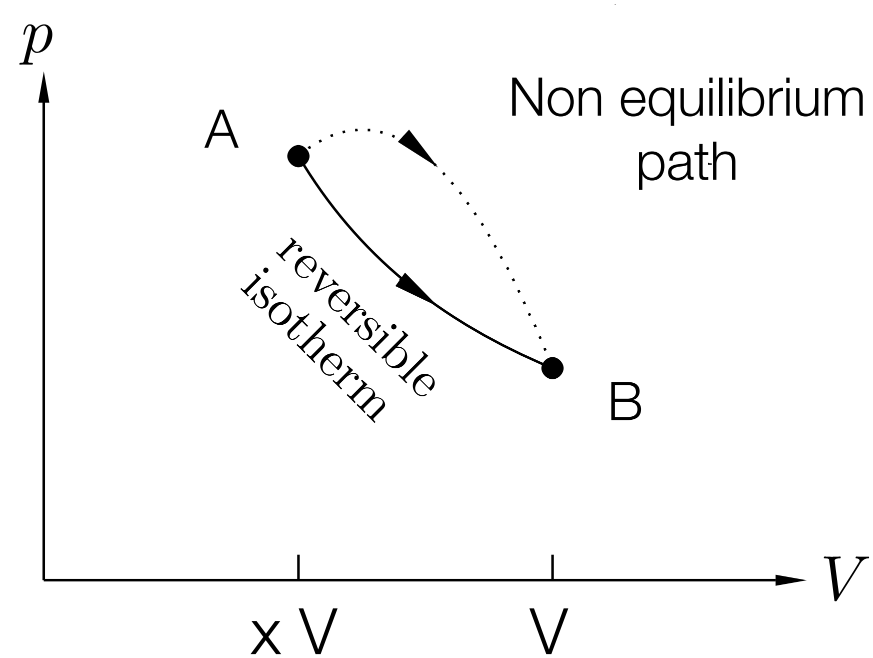


Fig. 14.6 Gas 1 is confined in a vessel of volume xV, while gas 2 is confined in a vessel of volume $(1-x)V$. Both gases are at pressure p and temperature T. Mixing occurs once the tap on the pipe connecting the two vessels is opened.

Computational strategy for finding the entropy change:
replace the non-equilibrium process with an equilibrium one



Similarly for gas 2

$$\Delta S_2 = \int_{(1-x)V_f}^{V_f} \frac{NkT}{VT}\, dV$$

$$= -N_2 k \ln(1-x)$$

So, finally since the initial temperatures and pressures are equal

$$p = \frac{NkT}{V}, \quad \text{so}, \quad N \propto V$$

And So

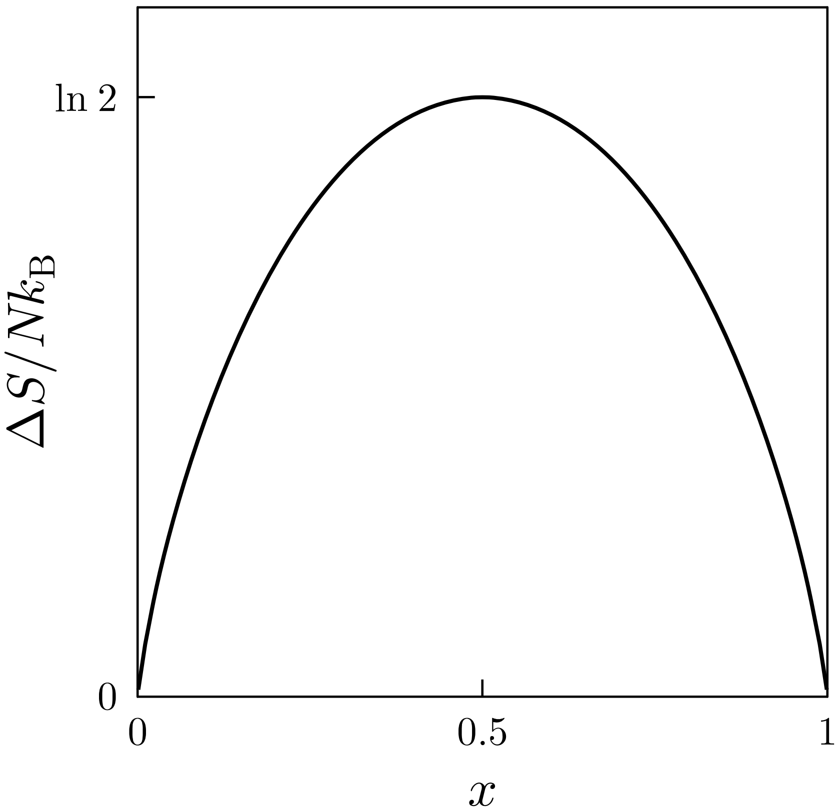
$$N_1 = x\,N \quad \text{and} \quad N_2 = (1-x)\,N$$

So $\frac{N_1}{N_2} = \frac{xV}{(1-x)V}$ and $N_1 + N_2 = N$

So finally

$$\boxed{\Delta S_{tot} = Nk\left(-x\ln x - (1-x)\ln(1-x)\right)}$$

A plot of this formula is shown below.



$$\frac{S}{Nk_B} = -x\log(x) - (1-x)\log(1-x)$$