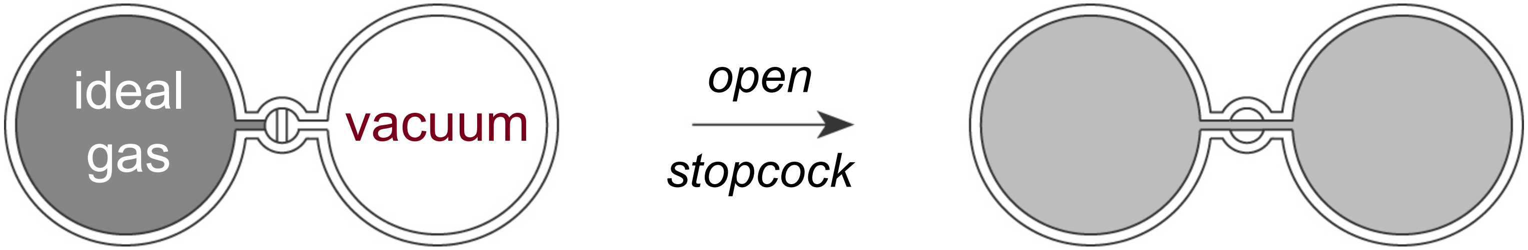
USING STATE FUNCTION CHARACTER



This is *not* a reversible process! But, because entropy is a *state function*, ΔS does *not* depend on the path.

Thus, we can use:

$$\Delta S = \int_1^2 \frac{\delta q_{rev}}{T} \qquad \delta q_{rev} = dU - \delta w_{rev}$$

$$dU \underset{\uparrow}{=} 0, \quad \delta q_{rev} = -\delta w_{rev}$$

isothermal

$$\Delta S = \int_1^2 \frac{\delta q_{rev}}{T} = -\int_1^2 \frac{\delta w_{rev}}{T}$$

$$\delta w_{rev} = -\frac{nRT}{V}\,dV$$

reversible

$$= nR\ln\frac{V_2}{V_1} > 0$$

IRREVERSIBLE VS REVERSIBLE

The difference is the change in entropy of *the surroundings*

Reversible case:

isothermal

$$\Delta U = 0$$

The gas *absorbs heat from the surroundings*, so *the entropy of the surroundings decreases*.

$$q_{rev} = -w_{rev} = nRT\ln\frac{V_2}{V_1}$$

$$\Delta S_{surr} = -\frac{q_{rev}}{T} = -nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{total} = S_{sys} + S_{surr} = 0$$

No change in *total* entropy, as expected for a reversible process

IRREVERSIBLE VS REVERSIBLE

The difference is the change in entropy of *the surroundings*

Irreversible case (stopcock opened all at once)**:**

$\Delta U = 0$ ← *isothermal*

No heat is transferred from the surroundings, so *the entropy of the surroundings is unchanged*.

$P_{ext} = 0, \text{so } w_{irr} = 0, \text{so } q_{irr} = 0$

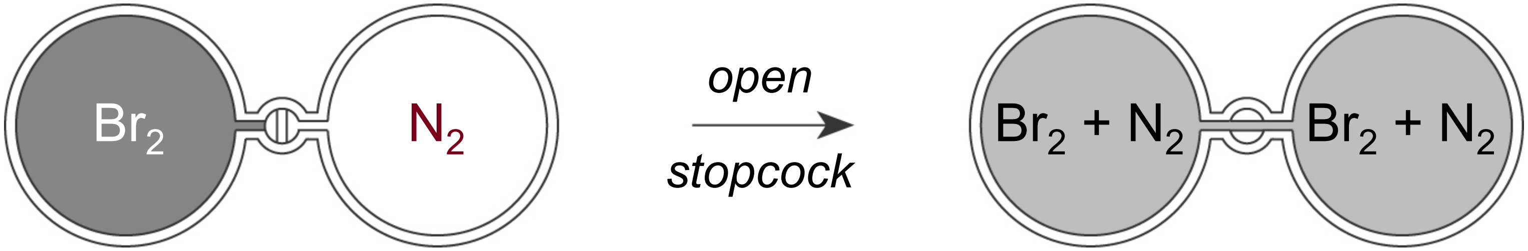
$\Delta S_{surr} = 0$

$$\Delta S_{total} = S_{sys} + S_{surr} = nR\ln\frac{V_2}{V_1} + 0 = nR\ln\frac{V_2}{V_1}$$

Total entropy *increases*, as expected for an irreversible process

Technical note: we used the irreversible *heat to compute the change in entropy of the surroundings. This is valid because there is zero work, so heat becomes a state function*

ENTROPY OF MIXING



For each gas i,

$$\Delta S_i = n_i R \ln \frac{\sum_j V_{j,0}}{V_{i,0}} = -n_i R \ln \frac{V_{i,0}}{\sum_j V_{j,0}}$$

where $V_{j,0}$ is the original volume occupied by gas j

But for ideal gases at the same T, V is proportional to n

$$\Delta S_i = -n_i R \ln \frac{n_i}{\sum_j n_j} \qquad \Delta S_{\text{mix}} = -R \sum_i n_i \ln y_i$$

where,

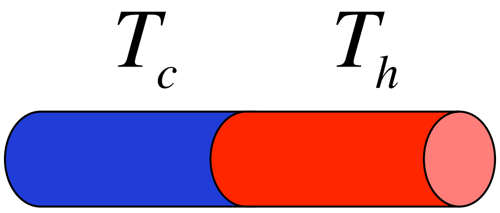
$$y_i = \frac{n_i}{\sum_j n_j}$$

mole fraction

always greater than zero, so mixing is spontaneous

METAL BAR TEMPERATURE EQUILIBRATION

Heat transfer between two identical pieces of the same material



Since no work (negligible ΔV):

$$\delta q_{\text{rev}} = dU = dq = C_V dT$$

If C_V is independent of T:

$$\Delta q = C_V\left(T_f - T_i\right)$$

Heat lost equal/opposite to heat gained:

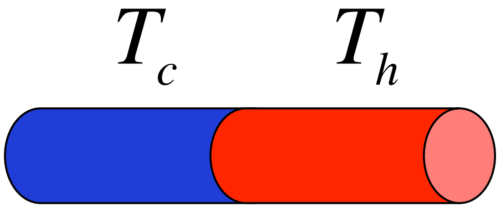
$$C_V\left(T_f - T_h\right) = -C_V\left(T_f - T_c\right)$$

$$\Rightarrow T_f = \left(T_c + T_h\right)/2$$

$$\Delta S = \int_{T_i}^{T_f} \frac{dq}{T} = C_V \int_{T_i}^{T_f} \frac{dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right)$$

METAL BAR TEMPERATURE EQUILIBRATION

Heat transfer between two identical pieces of the same material



$$\boxed{\Delta S = \int_{T_i}^{T_f} \frac{dq}{T} = C_V \int_{T_i}^{T_f} \frac{dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right)}$$

The cold rod:

$$\Delta S = C_V \ln\left(\frac{T_c + T_h}{2T_c}\right)$$

The hot rod:

$$\Delta S = C_V \ln\left(\frac{T_c + T_h}{2T_h}\right)$$

Total: *Spontaneous?*

$$\Delta S = C_V \ln\left[\frac{\left(T_c + T_h\right)^2}{4T_cT_h}\right]$$

$$(T_c - T_h)^2 > 0$$

$$T_c^2 - 2T_cT_h + T_h^2 > 0$$

$$T_c^2 + 2T_cT_h + T_h^2 > 4T_cT_h$$

$$(T_c + T_h)^2 > 4T_cT_h \quad ✔$$