Examples of entropy changes

Heating water

Take a mass *m* of water from 0°C to 100°C.

Because entropy is a function of state we can consider any convenient reversible path.

Consider the following quasistatic process. When water at T is heated to $T + dT$ the heat entering the water reversibly is

$$dQ_R = m\,c\,dT$$

where c is the **specific heat capacity**.

The total change in entropy is

$$\Delta S = \int_i^f \frac{dQ_R}{T} = \int_i^f \frac{mc}{T} dT$$

$$\Delta S = \int_{273}^{373} \frac{mc}{T} dT$$

$$\Delta S = mc \ln\left(\frac{373}{273}\right)$$

Examples of entropy changes

Phase change

Convert a mass *m* of water into steam at 100°C.

At the boiling point T is constant, and so

$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{Q}{T} = \frac{ml_V}{373}$$

where l_V is the **specific latent heat of vaporisation**.

Note:
Phase transformations are only reversible at precisely the transition temperature.

Examples of entropy changes

Carnot engine

In a cyclic process $\Delta S(system) = 0$

$$\Delta S(hot\ reservoir) = -\frac{Q_1}{T_1}$$

$$\Delta S(cold\ reservoir) = +\frac{Q_2}{T_2}$$

So the total entropy change of the universe is

$$\Delta S(system + surroundings) = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0$$

Consider an irreversible engine operating between T_1 and T_2 and having the same Q_1.

The lower efficiency would mean a larger Q_2, and then

$$\Delta S > 0$$

Examples of entropy changes

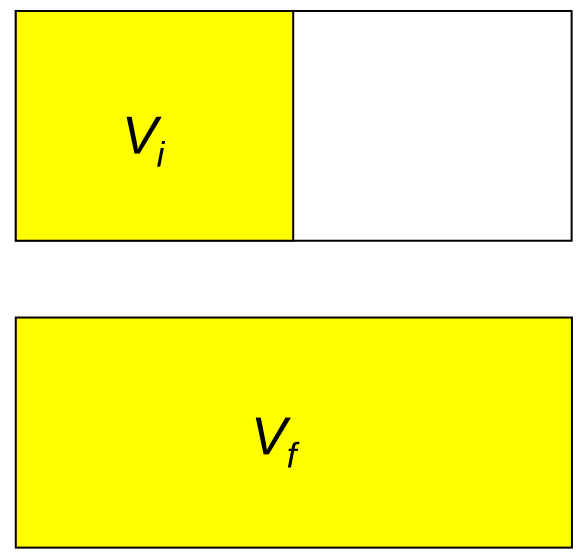
Free expansion

Since $Q = W = 0$, $\Delta U = 0$, and if ideal gas $\Delta T = 0$.
To calculate ΔS(gas) choose reversible path $i \rightarrow f$.
Quasistatic isothermal expansion gives
$\Delta U = 0$ again but now $Q = -W \neq 0$.

$$\Delta S(system) = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int_i^f -dW = \frac{1}{T}\int_i^f PdV$$

$$\Delta S(system) = \frac{1}{T}\int_i^f \frac{nRT}{V}dV = nR\ln\left(\frac{V_f}{V_i}\right)$$

This is necessarily positive since $V_f > V_i$.
ΔS(system) > 0 despite Q=0 in actual process.
ΔS(surroundings) = 0.



ΔS(system+surroundings) > 0
(**irreversible process**)

Examples of entropy changes

Heat transfer

(a) From system A to B, both at T

$$\Delta S_A = -\frac{\Delta Q}{T}$$

$$\Delta S_B = +\frac{\Delta Q}{T}$$

$$\Delta S(universe) = 0$$

as expected for reversible heat transfer with infinitesimal temperature difference.

(b) From system A at T_A to system B at T_B, with significant temperature differential $T_A > T_B$

$$\Delta S_A = -\frac{\Delta Q}{T_A}$$

$$\Delta S_B = +\frac{\Delta Q}{T_B}$$

$$\Delta S(universe) > 0$$

This process is irreversible due to non-zero temperature differential.