The thermodynamic definition of entropy

Atkins, Chapter 4

$$\Delta S_{Sys} = \frac{q_{rev}}{T}$$

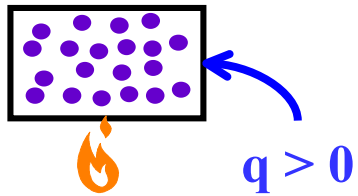
heat that would be transferred in a reversible process (= maximum heat)

temperature at which heat exchange takes place

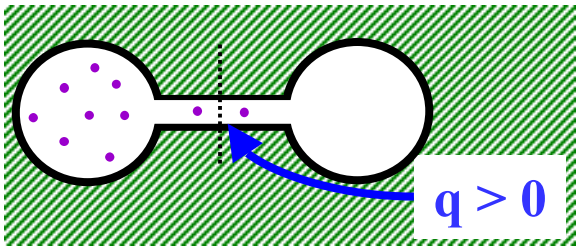
$$dS_{Sys} = \frac{dq_{rev}}{T}$$

small change

Why is this a suitable definition?

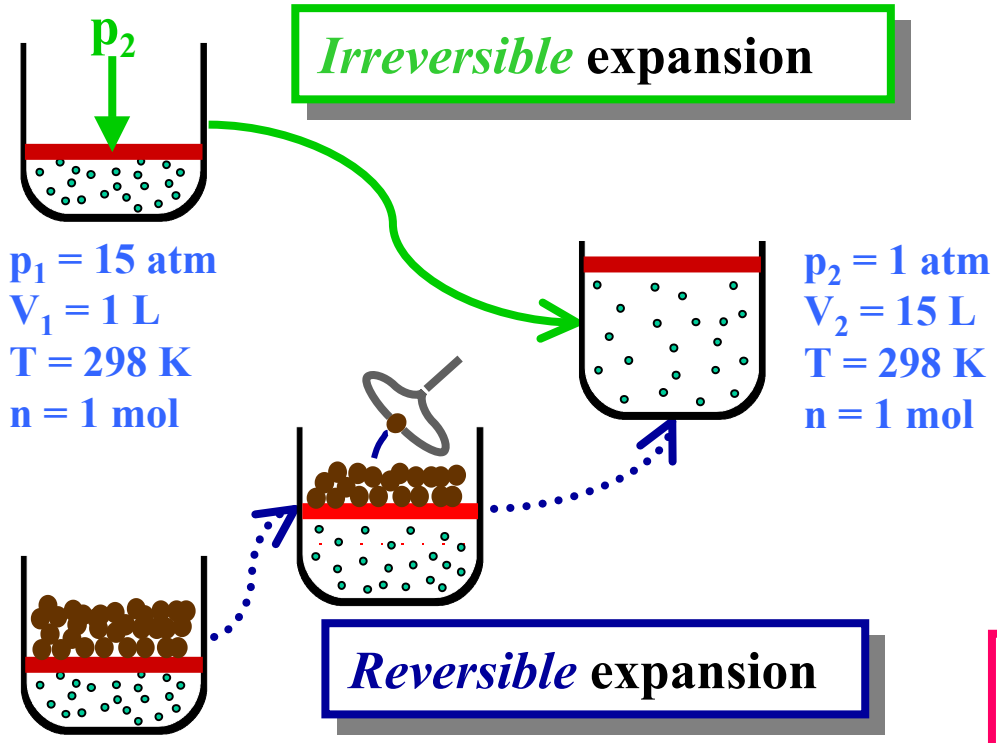


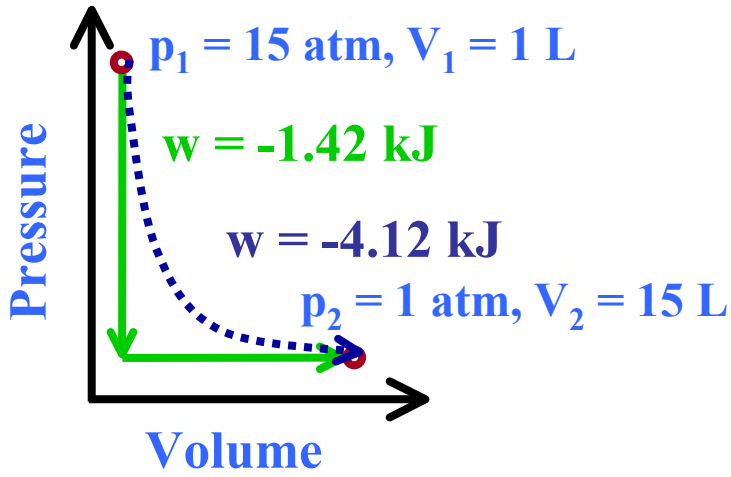
Adding heat increases the entropy (and disorder) of the system



The entropy (and disorder) of the system increases in an isothermal expansion

Entropy change in a system can be calculated from the reversible heat





$$w_{rev} = -nRT \ln\left(\frac{V_2}{V_1}\right) = -4.12\ \text{kJ}$$

The system entropy increases by the same amount in both expansions (state function!)

$q_{rev} = -w_{rev} = +4.12$ kJ $\Rightarrow$ $\Delta S = \dfrac{q_{rev}}{T} = \dfrac{4.12\ \text{kJ}}{298.15 K} = 13.8\ J\ K^{-1}$

How do classical and statistical thermodynamic definitions of ΔS_{Sys} match?

Classical thermodynamic definition of S in the isothermal expansion of a perfect gas:

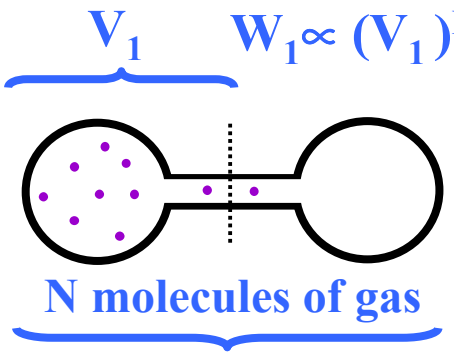
$$\Delta S = S_2 - S_1 = \int_{state1}^{state2} \frac{dq_{rev}}{T} = \frac{1}{T}\int_{state1}^{state2} dq_{rev} = \frac{q_{rev}}{T};\ \ w_{rev} = -nRT\ln\left(\frac{V_2}{V_1}\right) = -q_{rev}$$

isothermal $\Rightarrow$ $\Delta U = q + w = C_v\,\Delta T = 0$

$\Rightarrow$ $$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

classical and statistical entropy change in the isothermal expansion of a perfect gas

Statistical thermodynamic definition of S in the isothermal expansion of a perfect gas:



$$\Delta S = k \ln W_2 - k \ln W_1 = k \ln (V_2)^N - k \ln (V_1)^N$$

$$\Delta S = k\ln\left(\frac{V_2}{V_1}\right)^N = Nk\ln\left(\frac{V_2}{V_1}\right) = nN_A k\ln\left(\frac{V_2}{V_1}\right)$$

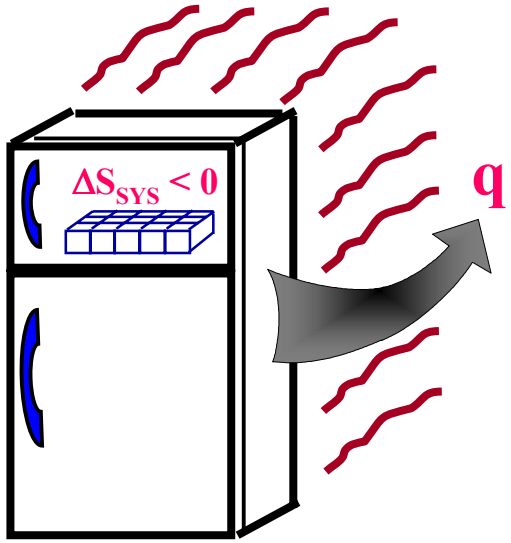
R

$\Rightarrow$ $$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

The second law of thermodynamics

$$\Delta S_{Universe} = \Delta S_{System} + \Delta S_{Surroundings} \geq 0$$

The net entropy will increase or stay the same. It will never decrease.



$\Delta S_{Surr} > 0$

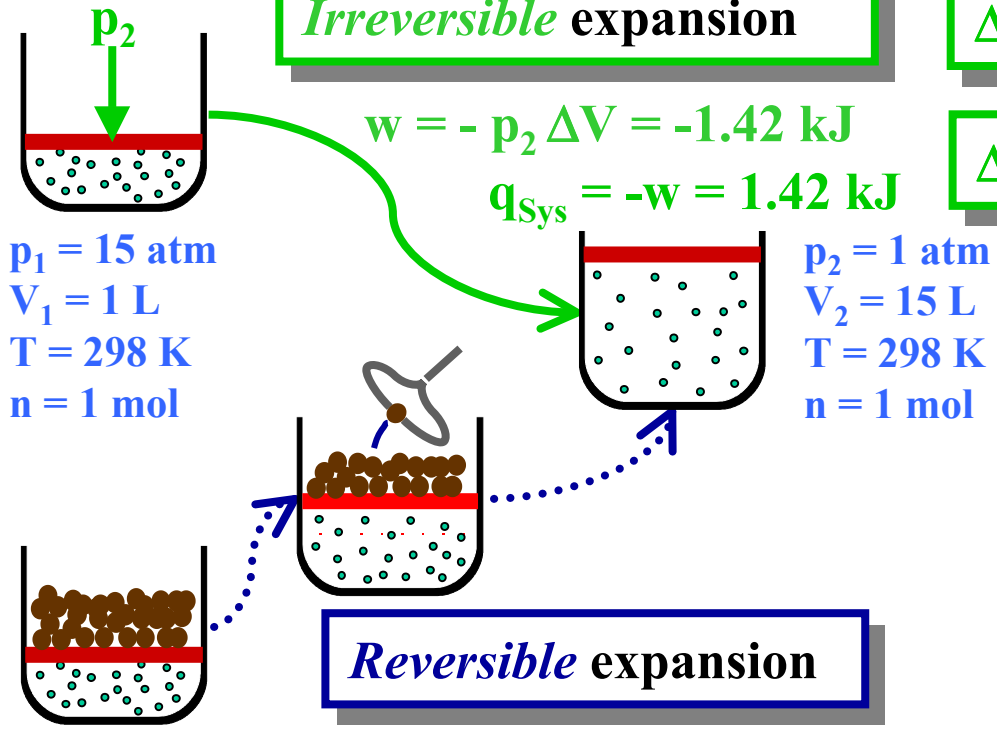
$\Delta S_{Surr} \geq \frac{q}{T}$

$\Delta S_{Univ} = 0$ only for a reversible process

$\Delta S_{Univ} > 0$ for all other processes

Atkins: The entropy of the universe tends to increase

ΔS_{Sys} is a state function, while ΔS_{Surr} and ΔS_{Univ} are pathway dependent



Irreversible **expansion**

$w = - p_2 \Delta V = -1.42$ kJ

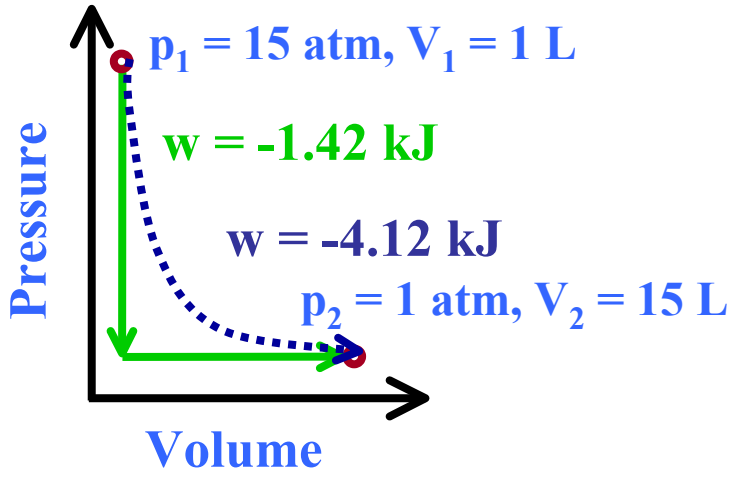
$q_{Sys} = -w = 1.42$ kJ

$\Delta S_{Sys} = 13.8$ J K^{-1}

$\Delta S_{Surr} = -4.8$ J K^{-1}

$\Delta S_{Univ} = 9$ J K^{-1}

Reversible **expansion**



$$w_{rev} = -nRT \ln\left(\frac{V_2}{V_1}\right) = -4.12 \text{ kJ} = -q_{rev} = -q_{Sys}$$

$$\Delta S_{Sys} = \frac{q_{rev}}{T}$$

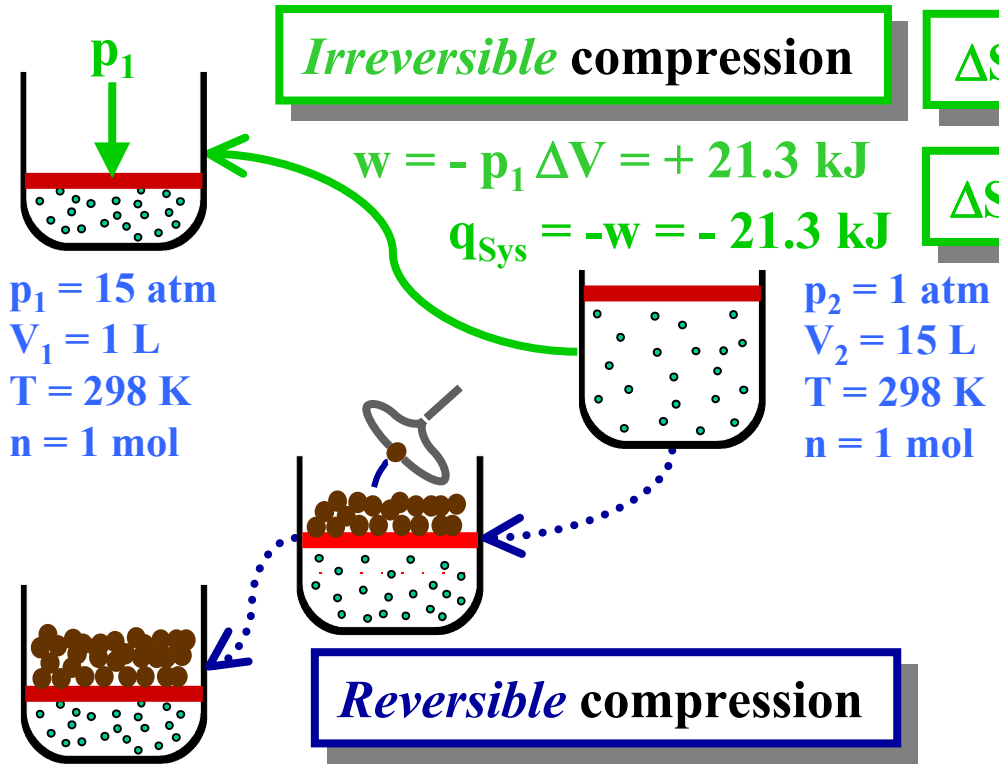
$$\Delta S_{Surr} = -\frac{q_{Sys}}{T}$$

$\Delta S_{Sys} = 13.8$ J K^{-1}

$\Delta S_{Surr} = -13.8$ J K^{-1}

$\Delta S_{Univ} = 0$ J K^{-1}

Isothermal compression



Irreversible compression

$w = -p_1 \Delta V = +21.3$ kJ

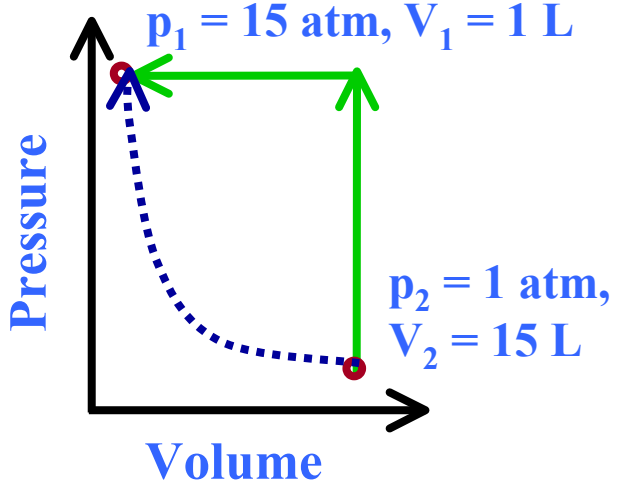
$q_{Sys} = -w = -21.3$ kJ

$\Delta S_{Sys} = -13.8$ J K^{-1}

$\Delta S_{Surr} = +71.4$ J K^{-1}

$\Delta S_{Univ} = 57.6$ J K^{-1}

Reversible compression



$$w_{rev} = -nRT \ln\left(\frac{V_1}{V_2}\right) = +4.12 \text{ kJ} = -q_{rev} = -q_{Sys}$$

$$\Delta S_{Sys} = \frac{q_{rev}}{T}$$

$$\Delta S_{Surr} = -\frac{q_{Sys}}{T}$$

$\Delta S_{Sys} = -13.8$ J K^{-1}

$\Delta S_{Surr} = +13.8$ J K^{-1}

$\Delta S_{Univ} = 0$ J K^{-1}