

Entropy Changes for Different Processes

6. Irreversible Processes:

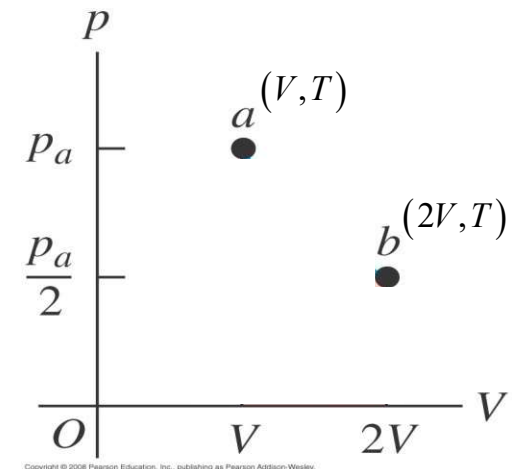
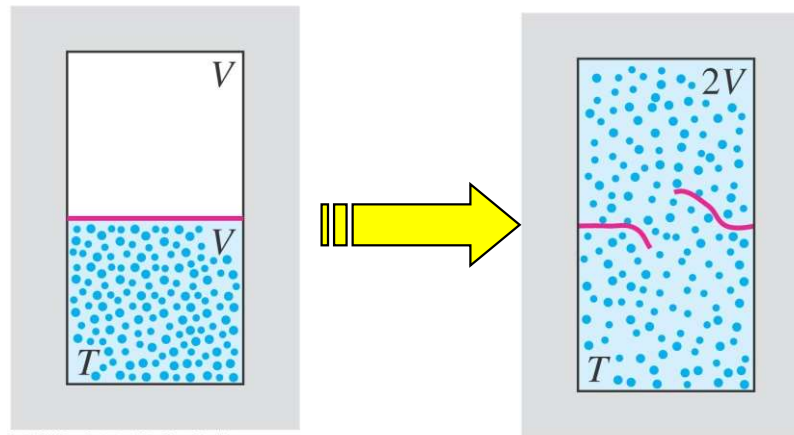
Although for a given *irreversible* process, we **cannot** write $dS = dQ_r/T$, ΔS between a well defined initial state a and final state b can still be calculated using a *surrogate* reversible process connecting a and b . (S is a state variable!)

Example 20.8: (adiabatic free expansion of an ideal gas)

Since $Q=W=0$, $\Delta U=0$.
For an ideal gas, this means that $\Delta T=0$ also.

Although $Q=0$, but ΔS is not zero!

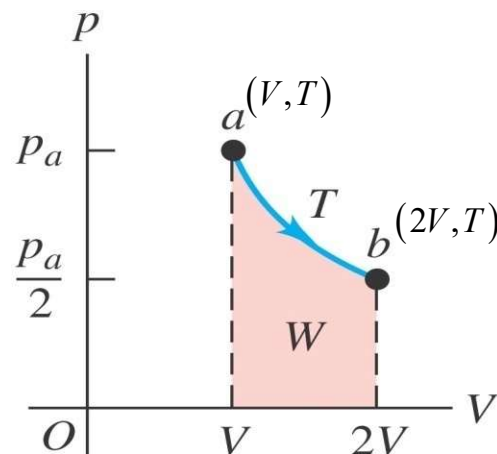
Initial State $a: (V, T)$ Final State $b: (2V, T)$



ΔS in an Adiabatic Free Expansion

Important point: Since S is a *state variable*, ΔS is the *same* for any processes connecting the same initial a and final b states.

In this case, since T does not change, we can use an *surrogate* isothermal process to take the ideal gas from state a (V, T) to state b ($2V, T$) to calculate ΔS .



Surrogate
Isothermal Expansion

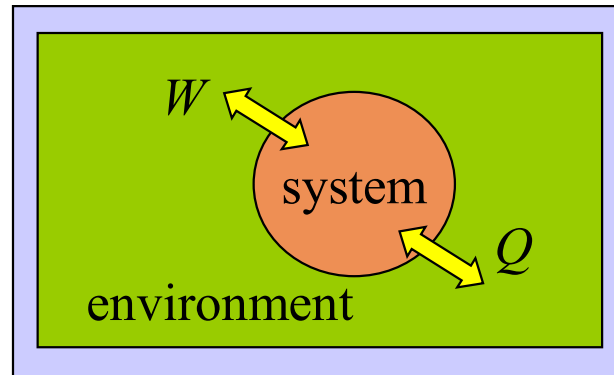
Applying our general formula to the surrogate isothermal expansion,

$$\Delta S = nC_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

we have,

$$\Delta S = nC_V \ln\left(\frac{T}{T}\right) + nR \ln\left(\frac{2V}{V}\right) = nR \ln 2 = 5.76 \text{ J / K} \quad (n=1)$$

2nd Law (Quantitative Form)



$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{env} \geq 0$$

$$(\Delta S_{tot} = 0 \text{ reversible}; \Delta S_{tot} > 0 \text{ irreversible})$$

“The *total* entropy (disorder) of an *isolated* system in any processes can never decrease.”

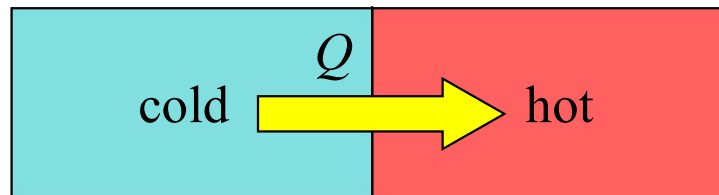
“Nature always tends toward the macrostate with the highest S (disorder) **[most probable]** in any processes.”

2nd Law ($\Delta S > 0$ & Clausius Statement)

Clausius Statement: Heat can't spontaneously transfer from T_C to T_H .

We will prove this by contradiction using $\Delta S_{\text{tot}} > 0$.

Assume the contrary,



$$\Delta S_H = \frac{+|Q|}{T_H} \quad (\text{heat absorbed into } T_H)$$

$$\Delta S_C = \frac{-|Q|}{T_C} \quad (\text{heat released by } T_C)$$

$$\Delta S_{\text{tot}} = \frac{+|Q|}{T_H} + \frac{-|Q|}{T_C}$$
$$\Delta S_{\text{tot}} = |Q| \left(\frac{1}{T_H} - \frac{1}{T_C} \right) \quad (T_H > T_C)$$

< 0

(with the explicit signs,
|Q| is taken to be +.)

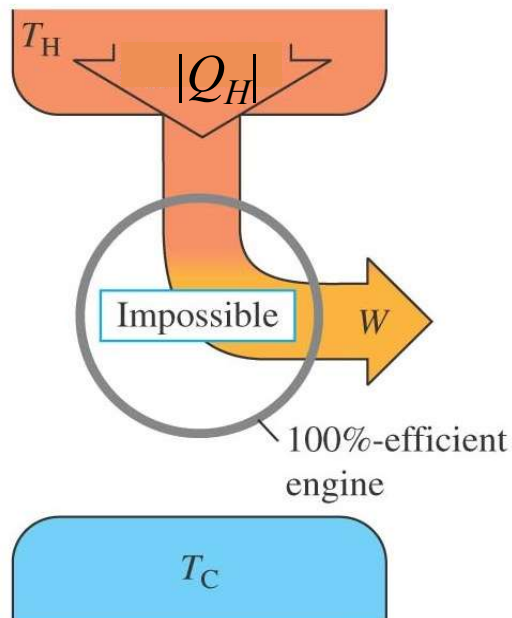
↑
Not Possible!
(violated $\Delta S_{\text{tot}} > 0$)

2nd Law ($\Delta S > 0$ & Kelvin-Planck Statement)

Kelvin-Planck Statement: No heat engine can convert heat from T_H completely into W .

We will prove this by contradiction again using the $\Delta S_{\text{tot}} > 0$.

Assume the contrary,



$$\Delta S_{\text{engine}} = 0 \quad (\text{engine operates in a cycle})$$

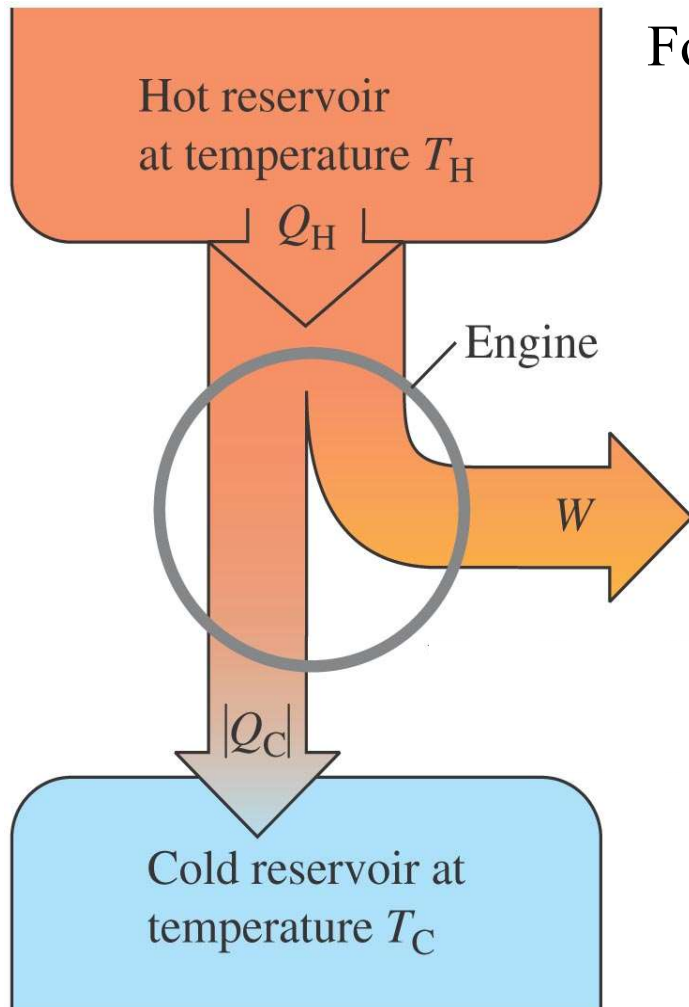
$$\Delta S_H = \frac{-|Q_H|}{T_H}$$

$$\Delta S_C = 0 \quad (\text{no heat exchange})$$

$$\text{So, } \Delta S_{\text{tot}} = \Delta S_{\text{engine}} + \Delta S_H + \Delta S_C = \frac{-|Q_H|}{T_H} < 0$$

Not Possible!
(again violated $\Delta S_{\text{tot}} > 0$)

2nd Law ($\Delta S > 0$ & Carnot Theorem)



For any reversible heat engines,

$$\Delta S_{engine} = 0$$

$$\Delta S_{env} = \frac{+|Q_C|}{T_C} + \frac{-|Q_H|}{T_H}$$

$$\Delta S_{tot} = \Delta S_{engine} + \Delta S_{env} = \frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H} \geq 0$$

2nd Law

→ $\frac{|Q_C|}{T_C} \geq \frac{|Q_H|}{T_H}$ or $\frac{|Q_C|}{|Q_H|} \geq \frac{T_C}{T_H}$

2nd Law ($\Delta S > 0$ & Carnot Theorem)

Consider the efficiency of a heat engine in general,

$$e \equiv 1 - \frac{|Q_C|}{|Q_H|}$$

Applying the inequality from the previous slide,

$$\frac{|Q_C|}{|Q_H|} \geq \frac{T_C}{T_H}$$

$$e = 1 - \frac{|Q_C|}{|Q_H|} \leq 1 - \frac{T_C}{T_H}$$

Recall that the efficiency of a Carnot Cycle is given by $e_{carnot} = 1 - \frac{T_C}{T_H}$.

This gives our desired result, $e \leq e_{carnot}$. Carnot engine is the most efficient!



Example: ΔS for some Reversible Processes in an Ideal Gas

One mole of monatomic gas doubles its volume . Calculate the entropy change if the expansion is done through i) a reversible isobaric process, ii) a reversible adiabatic process, and iii) a reversible isothermal process.

[link to solution](#)

<http://complex.gmu.edu/www-phys/phys262/soln/delsexample.pdf>

Example 20.6

1.00kg of water at 0°C is *slowly* (quasi-statically) heated to 100°C.
(no phase change) Calculate ΔS .

From each of the infinitesimal step, we have $dS = \frac{dQ}{T}$

$$\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{mc_w dT}{T}$$

$$= mc_w \ln\left(\frac{T_f}{T_i}\right)$$

$$= 1.00\text{kg} (4190\text{J} / \text{kg} \cdot \text{K}) \ln\left(\frac{100 + 273}{0 + 273}\right)$$

$$= 4190\text{J} / \text{K} (0.3121) = +1308\text{J} / \text{K} > 0$$

(Entropy increases as water get hotter and water molecules get more agitated.)

Entropy Changes for Different Processes

5. During Phase Changes (or other isothermal Processes):

$$\Delta S = \int \frac{dQ}{T} = \frac{1}{T} \int dQ \quad (T \text{ stays constant during a phase change.})$$

$$\Delta S = \frac{Q}{T} = \frac{mL}{T}$$

Example 20.10

1.00kg of water at 100°C is placed in thermal contact with 1.00kg of water at 0°C.

First, we can solve for T_f :



$$mc_w (T_{final} - T_h) + mc_w (T_{final} - T_c) = 0 \quad \rightarrow \quad T_{final} = \frac{T_h + T_c}{2} = 50^\circ C$$

Now, $\Delta S_{tot} = \Delta S_h + \Delta S_c$

$$\begin{aligned} &= mc_w \ln\left(\frac{T_{final}}{T_h}\right) + mc_w \ln\left(\frac{T_{final}}{T_c}\right) \\ &= 1.00kg (4190J / kg \cdot K) \left(\ln\left(\frac{50 + 273}{100 + 273}\right) + \ln\left(\frac{50 + 273}{273}\right) \right) \\ &= 4190J / K (-0.1439 + 0.1682) = +102J / K > 0 \end{aligned}$$

Microscopic Interpretation of Entropy

Microstate vs. Macrostate:

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	

Macroscopic state	Corresponding microscopic states
Two heads, two tails	
One head, three tails	
Four tails	

Two heads,
two tails



Recall:

Macrostate: a bulk description of a system in terms of its macroscopic variables.

One head,
three tails



Four tails



Microscopic Interpretation of Entropy

Microstate vs. Macrostate:

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	

Recall:

Macrostate: a bulk description of a system in terms of its macroscopic variables.

Microstate: a specific description of the properties of the individual constituent of the system.

Macroscopic state	Corresponding microscopic states
Two heads, two tails	
One head, three tails	
Four tails	



Microscopic Interpretation of Entropy

Observations:

1. For a given macrostate, typically there are many possible microstates!

(If the # of coins (or molecules) is large ($\sim N_A$), the # of microstates corresponding to a particular macrostate can be astronomically large.)

2. All individual microstates are equally likely.

(Each coin has exactly 50% being head or tail and each toss is independent.)

Microscopic Interpretation of Entropy

Observations:

3. However, for a given macrostate, the # of possible microstates are different!

→ Since all microstates are equally likely, the probability for different macrostates is different.

4. Some macrostate are much more probable than others.

(When $N \sim N_A$, this disparity can be huge!)



Microscopic Interpretation of Entropy

Important Observations:

5. The *less probable* macrostates (all heads or all tails) correspond to *more ordered* microstates!
6. The *more probable* macrostates (50/50 heads and tails) correspond to the more *disordered* microstates.

Microscopic Interpretation of Entropy

These observations motivate the following microscopic definition of entropy:

$$S = k \ln W$$

Boltzmann's Equation

where W is the # of possible microstates for a given macrostate and k is the Boltzmann constant.

Example (4 coins):

macrostate (all heads)



of microstates = 1

$$S = k \ln 1 = 0$$

All matched coins (ordered)



macrostate (3 H & 1 T)

of microstates = 4

$$S = k \ln 4$$

unmatched coins (less order)