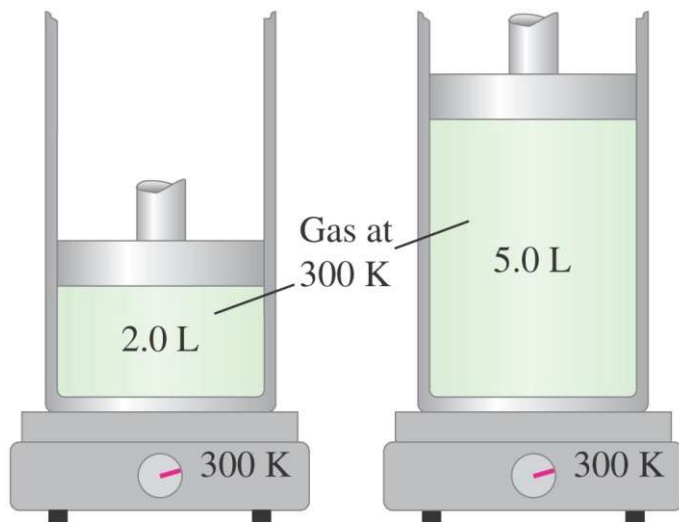


Entropy: Disorder

Recall that the 2nd Law of Thermodynamics is a statement on nature's preferential direction for systems to move toward the state of disorder.

Let see how **Entropy** is a quantitative measure of disorder.

From our previous derivation, the quantity dQ / T was from the **isothermal branch** of the infinitesimal Carnot cycle. Let look at an isothermal expansion of an ideal gas *microscopically*:



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Intuitively, as the gas expands into a bigger volume, the degree of randomness for the system increases since molecules now have more choices (spaces) for them to move around. One can associate the increase in randomness to the ratio:

$$\frac{\Delta V}{V} \quad \text{or} \quad \frac{dV}{V}$$

(Recall T stays the same \rightarrow avg. KE stays the same)

Entropy: Disorder

Since this is an isothermal process, we have the following relation from the 1st Law:

$$\begin{array}{l} dQ = dW = PdV = \frac{nRT}{V} dV \\ (dU = 0) \end{array} \quad \longrightarrow \quad \frac{1}{nR} \frac{dQ}{T} = \frac{dV}{V}$$

So, the newly introduced macroscopic variable S (entropy),

$$dS \equiv \frac{dQ}{T} \quad [S] = J / K$$

is a quantitative measure of the degree of disorder of the system.

dS is an infinitesimal entropy change for a reversible process at temperature T .
For any finite *reversible* process, the total entropy change ΔS is,

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

Entropy

$$dS \equiv \frac{dQ}{T}$$

and

$$\oint_{\text{cycle}} dS = \frac{dQ_r}{T} = 0$$

$$[S] = J / K$$

This state variable S is called the **entropy** of the system.

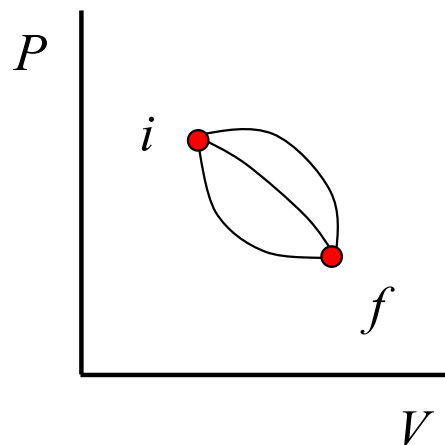
Entropy is macroscopic variable describing the degree of disorder of the system.

Entropy Changes for Different Processes

1. General *Reversible* Processes:

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

Note: S is a *state variable*, ΔS is the *same* for *all* processes (including **irreversible** ones) with the same initial and final states!



NOTE: in most applications, it is the change in entropy ΔS which one typically needs to calculate and not S itself.

Entropy Changes for Different Processes

2. Reversible Cycles:

$$\Delta S_{\text{cycle}} = \oint_{\text{cycle}} ds = \oint_{\text{cycle}} \frac{dQ_r}{T} = 0$$

3. **Any** Reversible Processes (not just cycles) for an Idea Gas:

$$(T_i, V_i) \rightarrow (T_f, V_f) \quad (\text{Note: Thru the Ideal Gas Law, } P \text{ is fixed for a given pair of } T \text{ \& } V.)$$

1st Law gives,

$$dU = dQ_r - dW$$

$$dQ_r = dU + dW = nC_V dT + PdV$$

$$dQ_r = nC_V dT + \frac{nRT}{V} dV$$

Entropy Changes for Different Processes

Dividing T on both sides and integrating,

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \int_i^f \left(\frac{nC_V dT}{T} + nR \frac{dV}{V} \right)$$

So, we have,

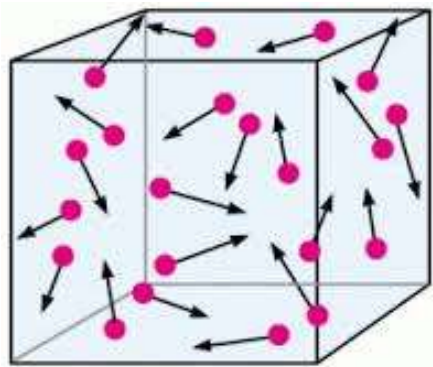
$$\Delta S = nC_V \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right)$$

Entropy: Disorder

(General Reversible Process)

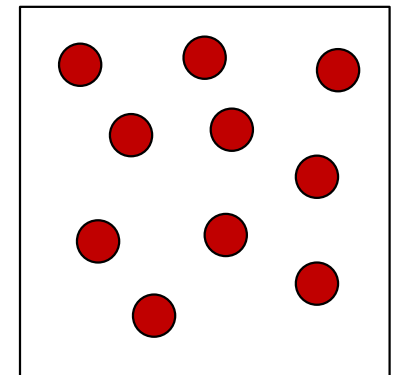
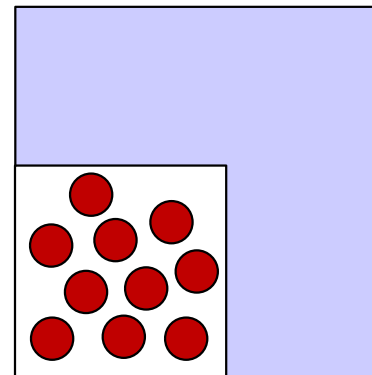
In our discussion of ΔS for an ideal gas through a **general** reversible process, we just derived the following relation,

$$dS = \frac{dQ_r}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$



$$\frac{dT}{T} \uparrow \Rightarrow S \uparrow$$

Thermal agitations



$$\frac{dV}{V} \uparrow \Rightarrow S \uparrow$$

Availability of space

Entropy Changes for Different Processes

4. Calorimetric Changes:

$$dQ = mcdT$$

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_i^f \frac{mcdT}{T}$$

If c is constant within temperature range, $\Delta S = mc \ln \left(\frac{T_f}{T_i} \right)$

If $c(T)$ is a function of T , $\Delta S = m \int_i^f \frac{c(T)dT}{T}$

Entropy Changes for Different Processes

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

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

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

Entropy Changes for Different Processes

6. Irreversible Processes:

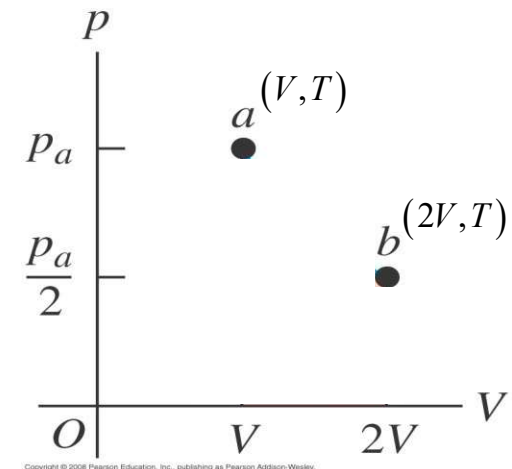
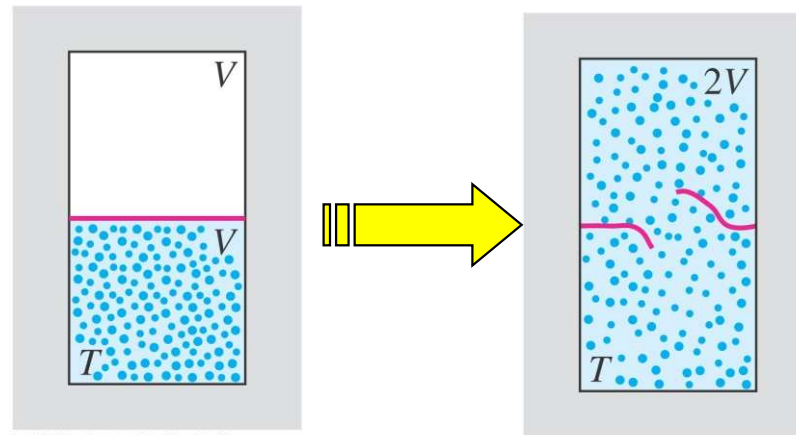
Although for a given *irreversible* process, we **cannot** write $dS = dQ_r/T$, ΔS between a well defined initial state a and final state b can still be calculated using a *surrogate* reversible process connecting a and b . (S is a state variable!)

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!

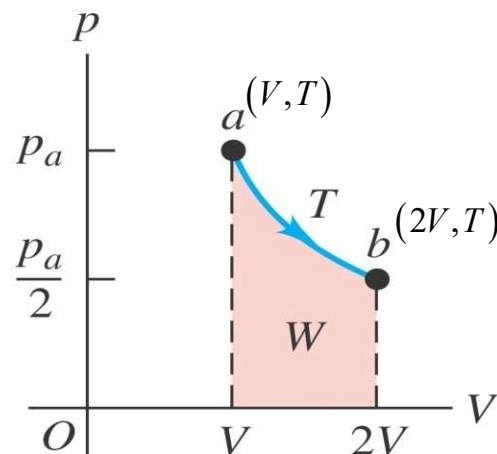
Initial State $a: (V, T)$ Final State $b: (2V, T)$



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

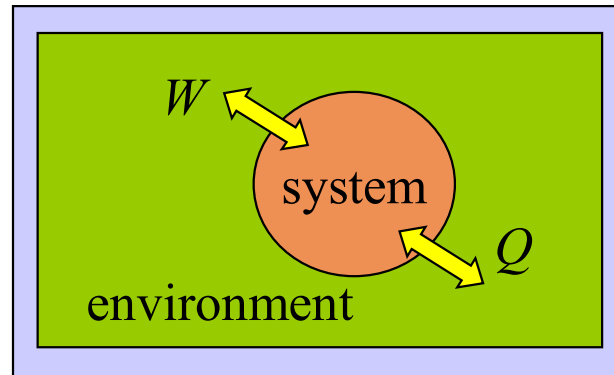
Applying our general formula to the surrogate isothermal expansion,

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

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.”

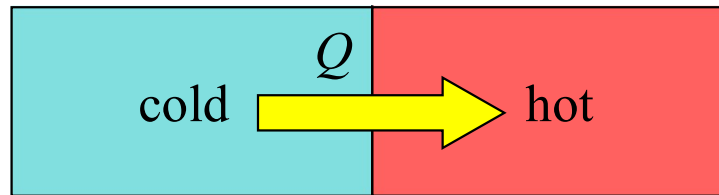
“Nature always tends toward the macrostate with the highest S (disorder) **[most probable]** in any processes.”

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,



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

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

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

< 0

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

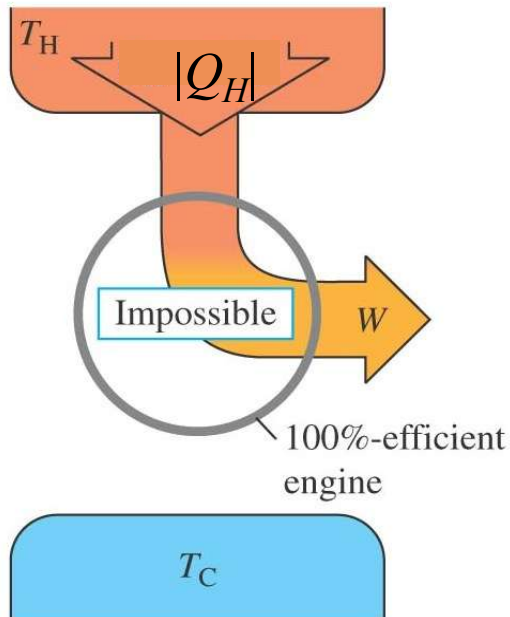
↑
Not Possible!
(violated $\Delta S_{\text{tot}} > 0$)

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,



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

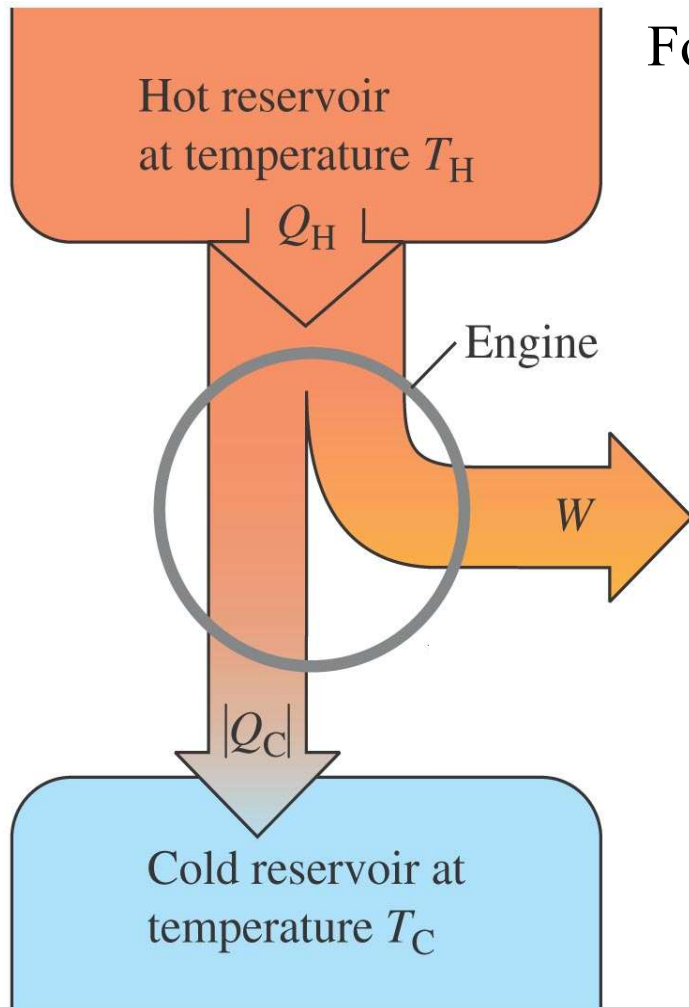
$$\Delta S_H = \frac{-|Q_H|}{T_H}$$

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

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

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.)

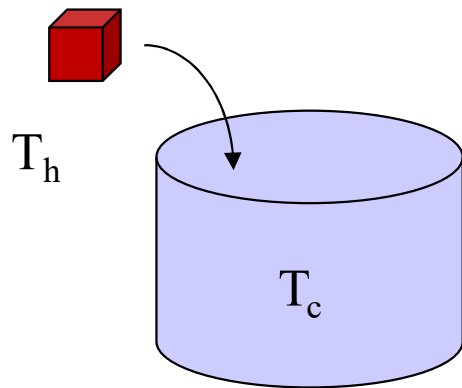
Entropy Changes for Different Processes

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

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

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

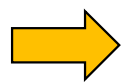
Example of an Irreversible Mixing Process



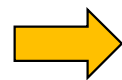
Heat exchange between two objects at *different* temperatures

Hot iron (at T_h) \rightarrow water bath (at T_c)

(MAKE IT SIMPLE : assume the heat from the hot iron is just hot enough to warm the water but not boiling any off \rightarrow reaching $T_c < T_{final} < T_h$)

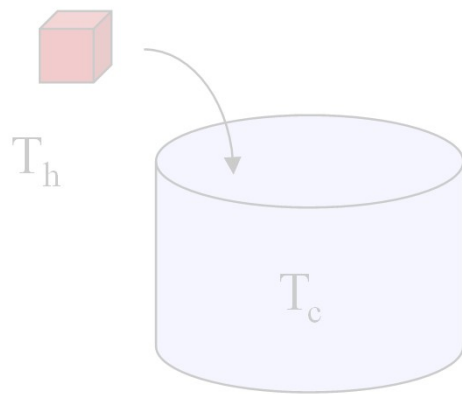


As soon as they are in thermal contact, heat Q will **spontaneously** flow between them until they reach thermal equilibrium.

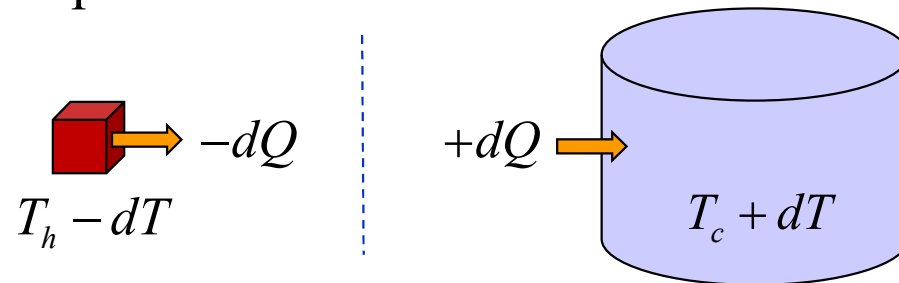


This process CANNOT be done quasi-statically!

Example of an Irreversible Mixing Process



However, *individually*, an infinitesimal dQ (in and out) of the individual objects can be calculated as a reversible process...

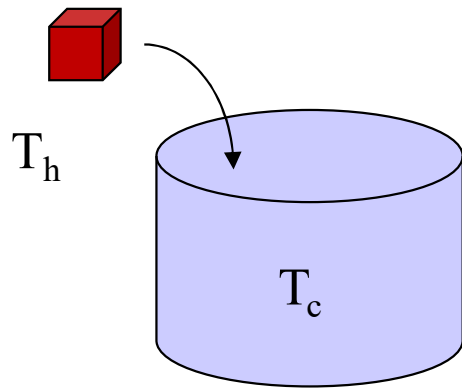


And, the *total* entropy change for this dT change is **positive** !

$$\begin{aligned}
 dS_{tot} &= dS_{hot} + dS_{cold} \\
 &= \frac{-m_i c_i dT}{T_h} + \frac{+m_w c_w dT}{T_c} \stackrel{\text{eng conservation}}{=} \frac{-dQ}{T_h} + \frac{+dQ}{T_c} = dQ \left(-\frac{1}{T_h} + \frac{1}{T_c} \right) > 0 \quad (\text{since } T_h > T_c)
 \end{aligned}$$

Note: Individually, S can be calculated by independent surrogate quasi-static processes raising and decreasing T slowly.

Example of an Irreversible Mixing Process



To be more general (not just infinitesimal change),

From 1st Law, we can solve for T_{final} from below:

$$m_{iron} c_{iron} (T_{final} - T_h) + m_{water} c_{water} (T_{final} - T_c) = 0$$

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

$$= m_{iron} c_{iron} \ln \left(\frac{T_{final}}{T_h} \right) + m_{water} c_{water} \ln \left(\frac{T_{final}}{T_c} \right)$$

$$= -m_{iron} c_{iron} \ln \left(\frac{T_h}{T_{final}} \right) + m_{water} c_{water} \ln \left(\frac{T_{final}}{T_c} \right)$$

$$> 0$$

Although it is not obvious from this expression that $\Delta S_{tot} > 0$, we know that it will be so from our argument on the previous page !

Let calculate ...

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 tail |  |

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)