

02. Thermodynamic Entropy

1. Clausius' Inequality
2. Thermodynamic Entropy

1. Clausius' Inequality

1854. "On a modified form of the second fundamental theorem in the mechanical theory of heat".

1865. "On several convenient forms of the fundamental equations of the mechanical theory of heat."

- Clausius' "Fundamental Principle" (1854):

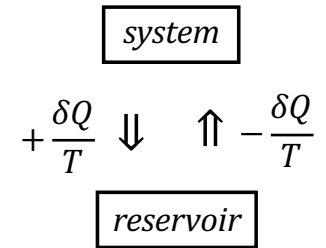


"Heat can never pass from a colder to a warmer body *without some other change, connected therewith, occurring at the same time.*"

Now formulate this "algebraically"...

- Consider a cyclic process involving infinitesimal transfers of heat $\delta Q/T$ between a system and a reservoir at lower temperature:

- Let $+\delta Q/T$ represent an emission of heat by the system to the reservoir.
- Let $-\delta Q/T$ represent an absorption of heat by the system from the reservoir.



"The algebraic sum of all the transformations which occur in a cyclical process can only be positive." (1854)

Or: $\oint \frac{\delta Q}{T} \geq 0$

Why? If the sum were negative, then the overall effect would be a passage of heat from lower to higher temp.

Moreover: If the process is reversible, then the sum is zero.

- It can't be negative.
- If it were positive, the process could be reversed to produce a negative result.

- 1865: Change of sign convention:

- Let $+\delta Q/T$ represent absorption of heat by the system.
- Let $-\delta Q/T$ represent emission of heat by the system.

$$\oint \frac{\delta Q}{T} \leq 0$$

Clausius' Inequality

- For reversible processes, let $dS = \delta Q_R/T$. Call S "entropy".

"... I propose to call the magnitude S the *entropy* of the body... I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable." (1865)



- For a thermally isolated system, can show that the 2nd Law entails:
$$\int_{\sigma_1}^{\sigma_2} dS = S(\sigma_2) - S(\sigma_1) \geq 0$$

What this means: For a thermally isolated system undergoing an energy transformation, the entropy of the final state σ_2 cannot be less than the entropy of the initial state σ_1 .



"... [W]e may express in the following manner the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat:

1. *The energy of the universe is constant.*
2. *The entropy of the universe tends to a maximum.*" (1865)

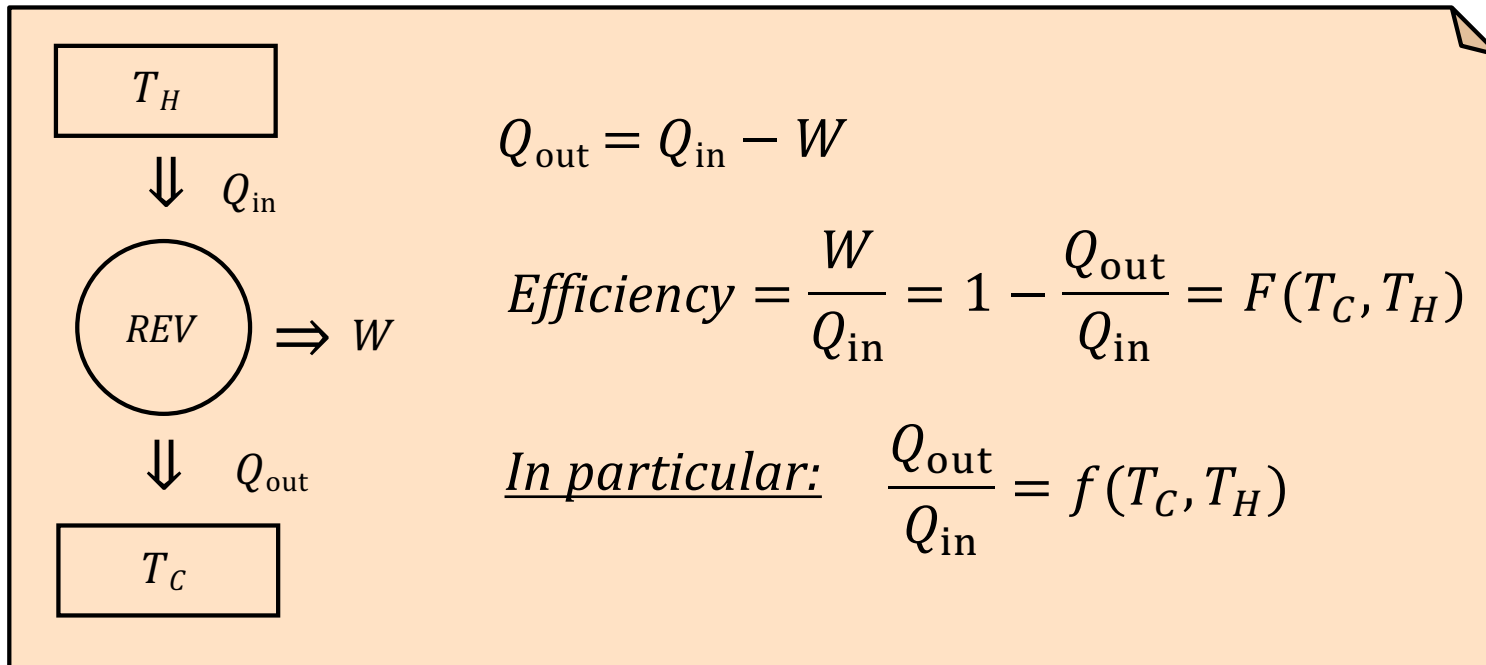
Contemporary Derivation of Clausius' inequality

- First: Let's derive the important relation for reversible heat engines

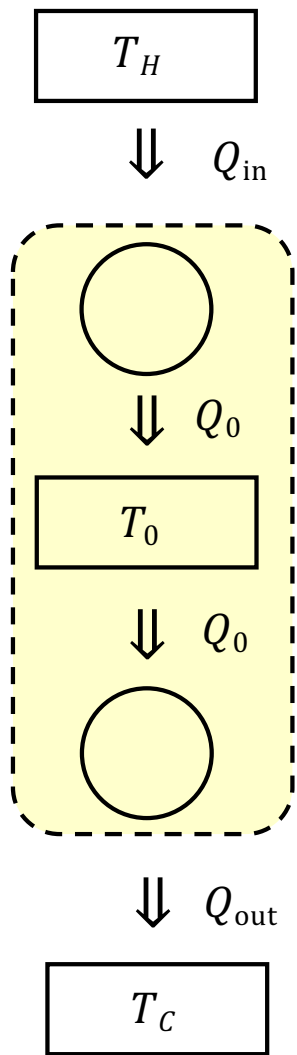
$$\frac{Q_{\text{out}}}{Q_{\text{in}}} = \frac{T_C}{T_H}$$

where the temperature is measured by the absolute Kelvin scale.

- Recall (Carnot's Claim #2): The efficiency of a reversible heat engine is a function *only* of the temperatures of the hot and cold places.



- Consider a multi-stage *reversible* heat engine:



- Note: $\frac{Q_{\text{out}}}{Q_{\text{in}}} = \frac{Q_{\text{out}}}{Q_0} \frac{Q_0}{Q_{\text{in}}}$

- So: $\frac{Q_{\text{out}}}{Q_{\text{in}}} = f(T_C, T_H) = f(T_C, T_0) \left(\frac{1}{f(T_H, T_0)} \right) = \frac{f(T_C)}{f(T_H)}$

- Now choose: $f(T_C) = T_C$, $f(T_H) = T_H$ ← Thomson's (1848) "absolute" temp scale.

- For this "Kelvin" temp scale, and for reversible heat engines:

$$\frac{Q_{\text{out}}}{Q_{\text{in}}} = \frac{T_C}{T_H}$$

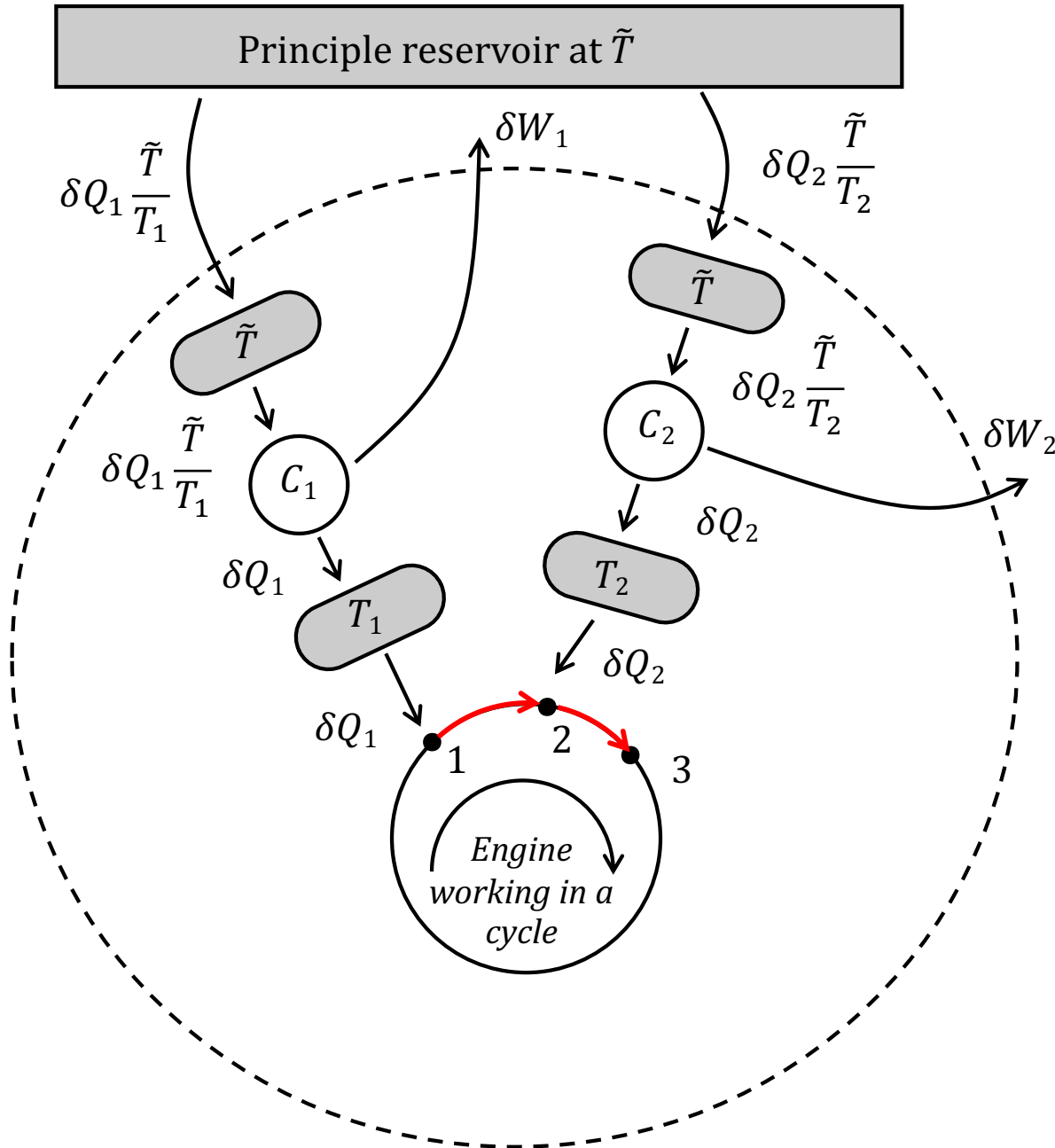
or

$$Q_{\text{in}} = Q_{\text{out}} \frac{T_H}{T_C}$$

Now: Let's derive Clausius' Inequality...

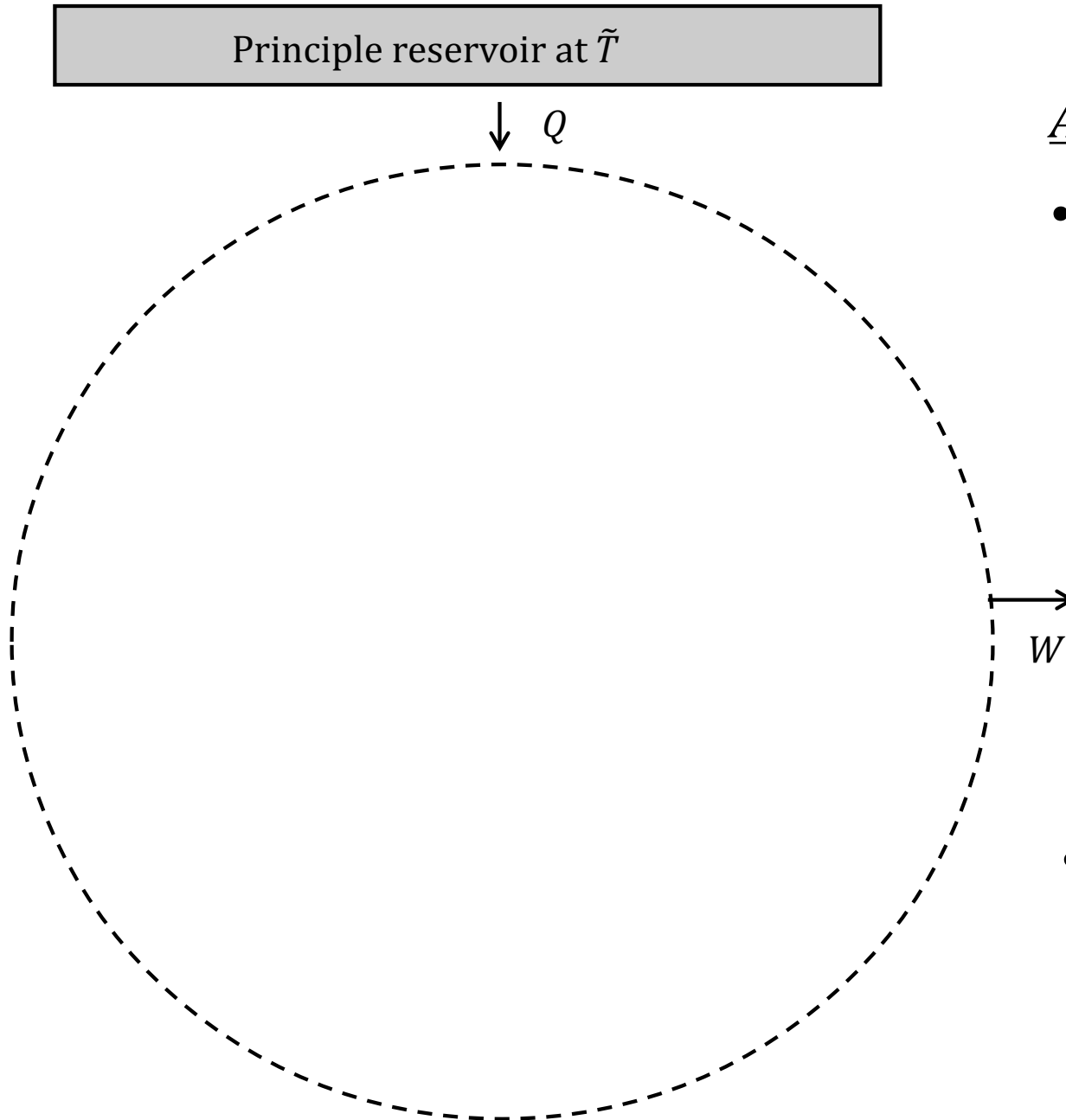
- Consider the following engine working in a cycle in which the initial and final states are identical.

$$Q_{\text{in}} = Q_{\text{out}} \frac{T_H}{T_C}$$



- Initial state 1 of working substance at temp T_1 .
- Use reservoir at T_1 to inject heat δQ_1 to move to state 2 at temp T_2 .
- Resupply T_1 using reversible heat engine C_1 , which takes heat $\delta Q_1(\tilde{T}/T_1)$ from reservoir at \tilde{T} , and performs work δW_1 .
- Resupply reservoir at \tilde{T} with heat $\delta Q_1(\tilde{T}/T_1)$ from principle reservoir.
- Repeat process.

- Consider the following engine working in a cycle in which the initial and final states are identical.



After complete cycle:

- Total heat supplied is

$$Q = \sum_i \delta Q_i \frac{\tilde{T}}{T_i}$$

- Total work output is

$$W = \sum_i \delta W_i$$


- $\Delta U = U_f - U_i = 0$

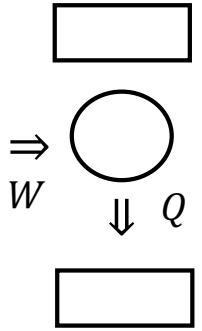
for a cycle

- So: $0 = -W + Q$

Or: $Q = W$

But! This is a violation of the 2nd Law (Thomson version)!

- So:
 - Either W and Q must be negative,  *work is done to the system and an equal amount of heat is extracted from it*
 - Or W and Q must be zero.



- Thus: $W = Q \leq 0$, or $\tilde{T} \sum_i \frac{\delta Q_i}{T_i} \leq 0$ or $\sum_i \frac{\delta Q_i}{T_i} \leq 0$

- Hence: $\oint \frac{\delta Q}{T} \leq 0$ *Clausius' Inequality*

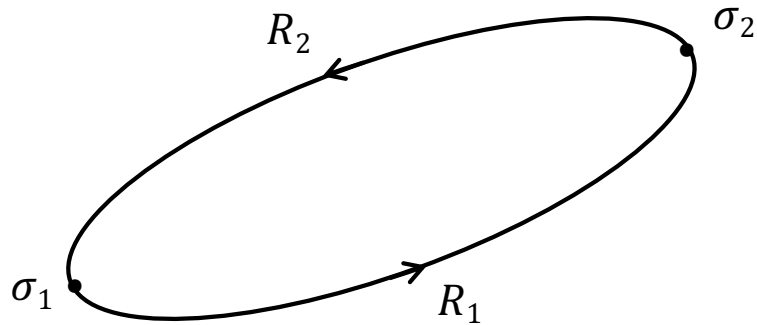
- What if the cycle is reversible?

- Then: $-\oint \frac{\delta Q_R}{T} \leq 0$ or $\oint \frac{\delta Q_R}{T} \geq 0$

- So: In order to be consistent with the first result, $\oint \frac{\delta Q_R}{T} = 0$.

2. Thermodynamic Entropy

- Consider a *reversible* cycle:



- Start in initial state σ_1 .
- Take reversible path R_1 to state σ_2 .
- Return to σ_1 via reversible path R_2 .

- Clausius' inequality is $\oint \frac{\delta Q_R}{T} = \int_{R_1}^{\sigma_2} \frac{\delta Q_R}{T} + \int_{R_2}^{\sigma_1} \frac{\delta Q_R}{T} = 0$

- Thus: $\int_{R_1}^{\sigma_2} \frac{\delta Q_R}{T} = - \int_{R_2}^{\sigma_1} \frac{\delta Q_R}{T} = \int_{R_2}^{\sigma_2} \frac{\delta Q_R}{T}$

- So: $\int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T}$ is *path-independent!*

- Which means: It can be represented by a path-independent function, call it S_{TD} :

$$\Delta S_{\text{TD}} = S_{\text{TD}}(\sigma_2) - S_{\text{TD}}(\sigma_1) \equiv \int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T}$$

*"thermodynamic
entropy"*

Def. 1 (*Thermodynamic entropy*). The **thermodynamic entropy** $S_{\text{TD}}(\sigma_2)$ of a state σ_2 is the ratio of the change in heat to temperature of a *reversible* process that connects an initial state σ_1 to σ_2 :

$$S_{\text{TD}}(\sigma_2) \equiv \int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T} + S_0 \quad \leftarrow \text{arbitrary constant}$$

Characteristics

1. Only defined for *reversible processes*; *i.e.*, processes that are "quasi-static".
 - *Quasi-static process* = succession of equilibrium states.
 - *Equilibrium state* = state of system in which macroscopic properties (*i.e.*, temp, volume, pressure, *etc.*) are constant.

2. Only defined for *equilibrium states*.

3. For infinitesimal changes in S_{TD} , can write

$$dS_{\text{TD}} = \delta Q_R / T$$

$1/T$ is an 'integrating factor' that converts a path-dependent function Q into a path-independent function S_{TD}

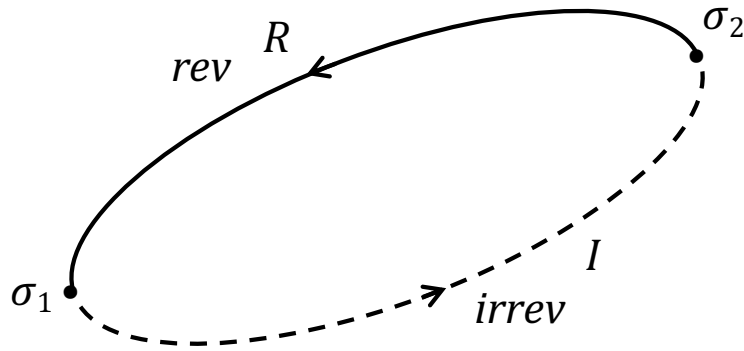
For an *irreversible* process connecting σ_1 and σ_2 , ΔS can still be calculated if there is, in principle, a reversible process that connects σ_1 and σ_2 .

Ex: Heating a beaker of water.

- *No reference to "disorder" or "chaos"!*
- *No reference to molecules or particles (gas or otherwise)!*
- *No reference to "information"!*

Principle of Increasing Thermodynamic Entropy

Consider an *irreversible* cycle:



Irreversible cycle consisting of an irreversible process I from σ_1 to σ_2 , followed by a reversible process R from σ_2 back to σ_1 .

- Clausius' inequality is $\int_I^{\sigma_2} \frac{\delta Q}{T} + \int_R^{\sigma_1} \frac{\delta Q_R}{T} < 0$ or $\int_I^{\sigma_2} \frac{\delta Q}{T} - \int_R^{\sigma_1} \frac{\delta Q_R}{T} < 0$

- Thus: $\Delta S = \int_R^{\sigma_2} \frac{\delta Q_R}{T} > \int_I^{\sigma_2} \frac{\delta Q}{T}$

← Note: If the cycle was reversible (i.e., if the path I was reversible), then $>$ would become $=$.

- So in general: $\Delta S = \int_R^{\sigma_2} \frac{\delta Q_R}{T} \geq \int_{\sigma_1}^{\sigma_2} \frac{\delta Q}{T}$

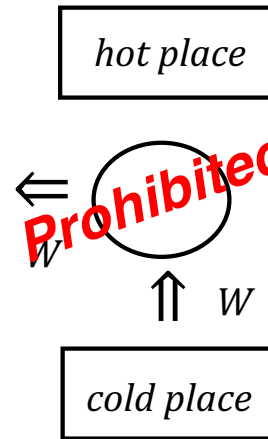
- Now: Suppose the path from σ_1 to σ_2 is *thermally isolated*; i.e., $\delta Q = 0$.

- Then: $S_{\text{TD}} \geq 0$ or $S_{\text{TD}}(\sigma_2) \geq S_{\text{TD}}(\sigma_1)$

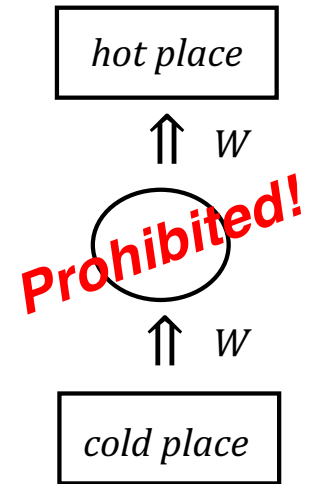
The entropy of a thermally isolated irreversible process increases, and is unaltered in a thermally isolated reversible process.

Summary of 2nd Law of Thermodynamics

(1) Clausius Form: No heat transfer from cold to hot place without work input:



(2) Thomson Form: No conversion of heat to work without exhaust:



Consequence of 2nd Law:

The *thermodynamic entropy* S_{TD} of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process.

Absolute statements!

Meant to hold for any system subject to thermodynamical analysis.

Summary of Entailments

