02. Thermodynamic Entropy S_{TD}

1. Clausius' Inequality

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

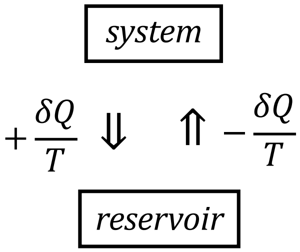
1865. "On several convenient forms of the fundamental equations of the mechanical theory of heat."

- *Clausius' "Fundamental Principle" (1854)*:

"Heat can never pass from a colder to a warmer body *without some other change, connected therewith*, occuring 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.*

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

Clausius' Inequality

- For reversible processes, let $dS_{\mathrm{TD}} = \delta Q_R/T$. Call S_{TD} "thermodynamic entropy".

> "... I propose to call the magnitude [S_{TD}] the [thermodynamic] *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:

$$\int_{\sigma_1}^{\sigma_2} dS_{\mathrm{TD}} = S_{\mathrm{TD}}(\sigma_2) - S_{\mathrm{TD}}(\sigma_1) \geq 0$$

What this means: For a thermally isolated system undergoing an energy transformation, the thermodynamic entropy of the final equilibrium state σ_2 cannot be less than the entropy of the initial equilibrium 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 [thermodynamic] entropy of the universe tends to a maximum.*"

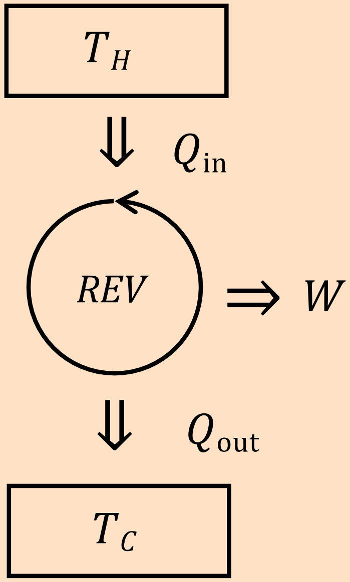
Aside: Contemporary Derivation of Clausius' inequality

- *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.

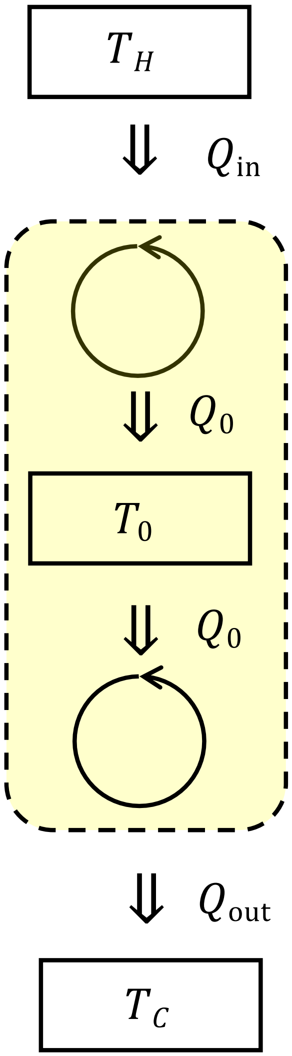


$$Q_{\text{out}} = Q_{\text{in}} - W$$

$$Efficiency = \frac{W}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} = F(T_C, T_H)$$

In particular: $$\frac{Q_{\text{out}}}{Q_{\text{in}}} = f(T_C, T_H)$$

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



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

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

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

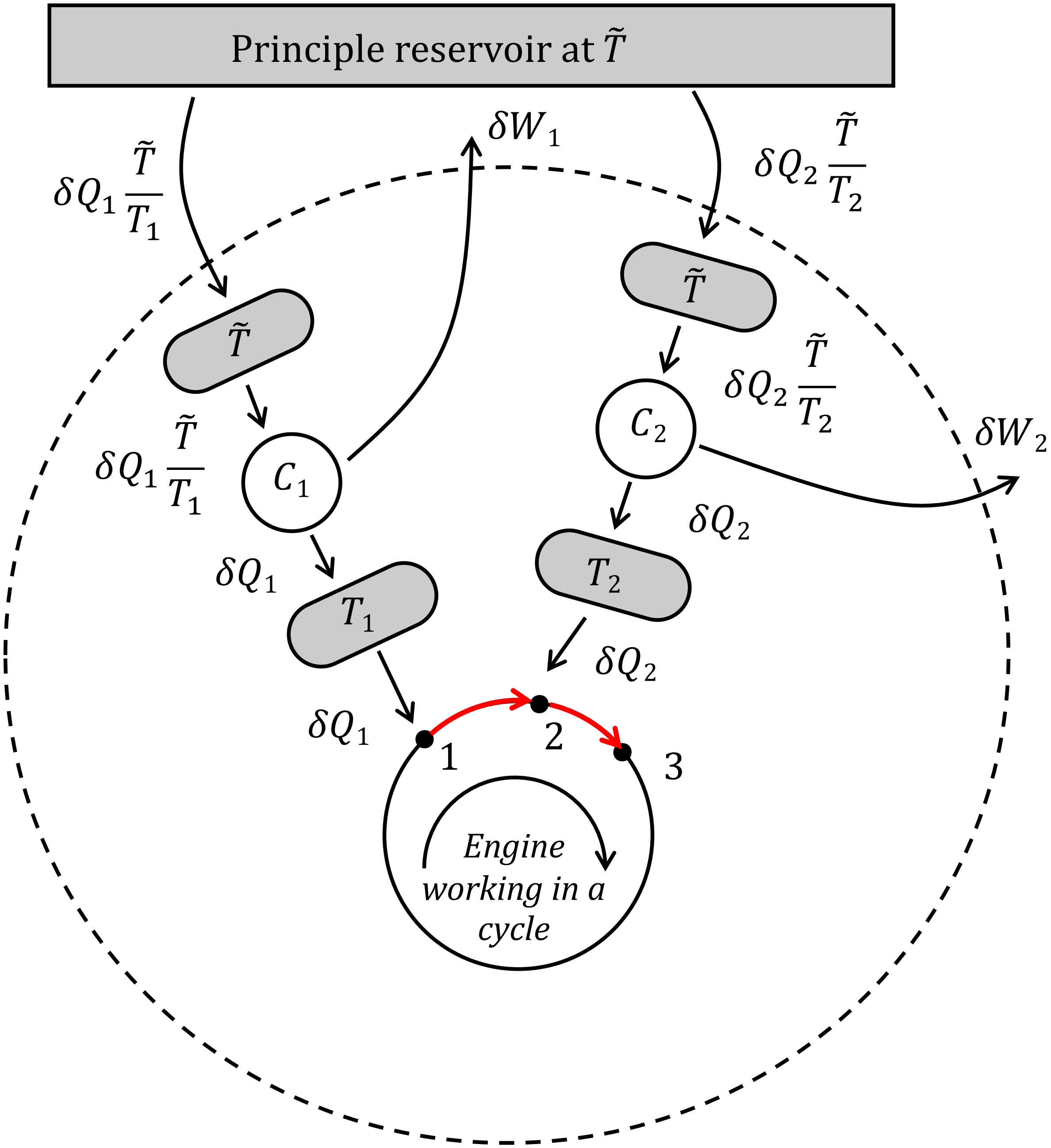
- *For this "Kelvin" temp scale, and for reversible heat engines*:

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

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

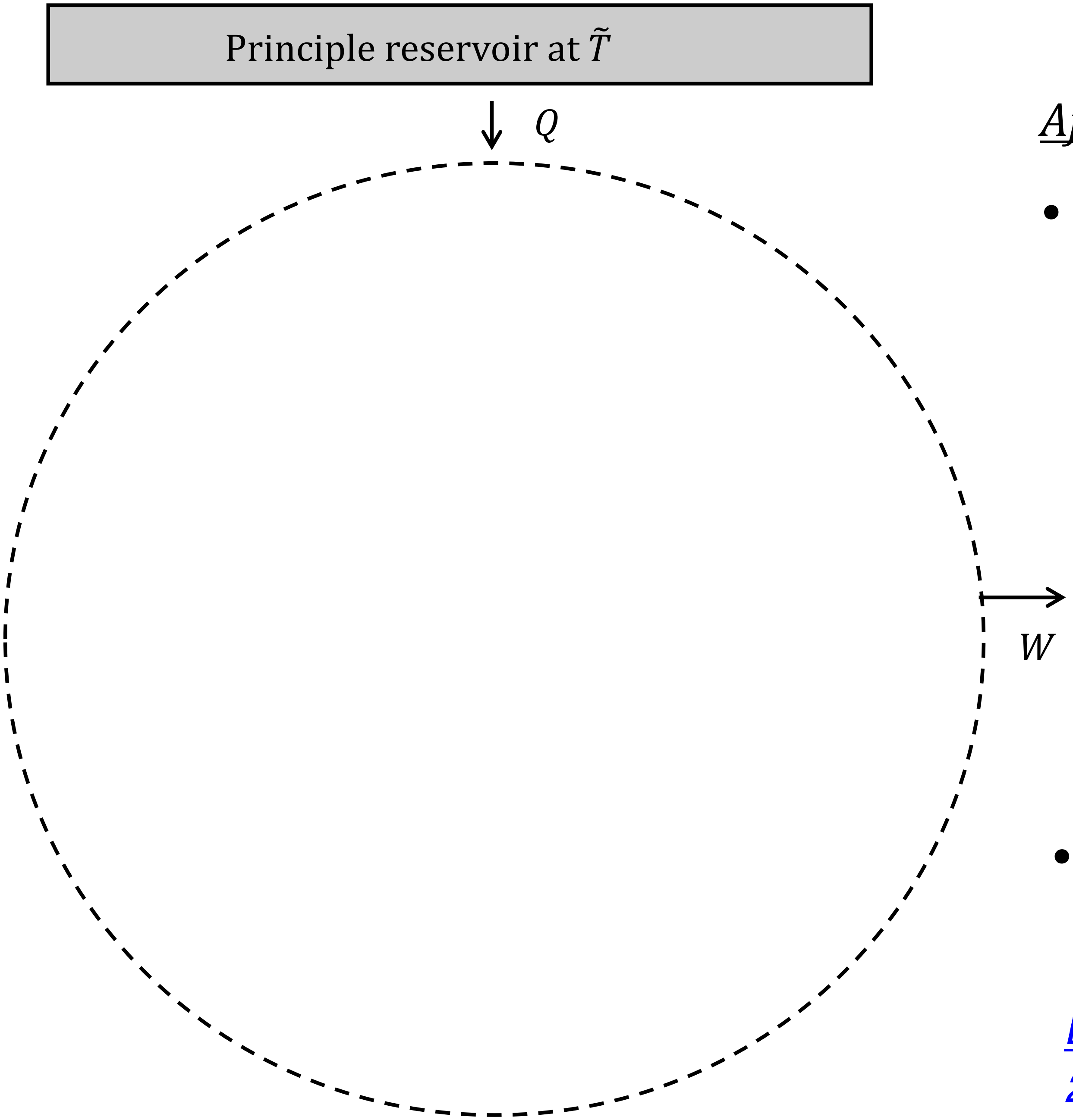
- Consider the following engine working in a cycle in which the initial and final states are identical.

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



- 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

$$W = \sum_i \delta W_i$$

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

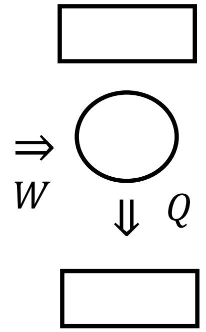
for a cycle

- *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.



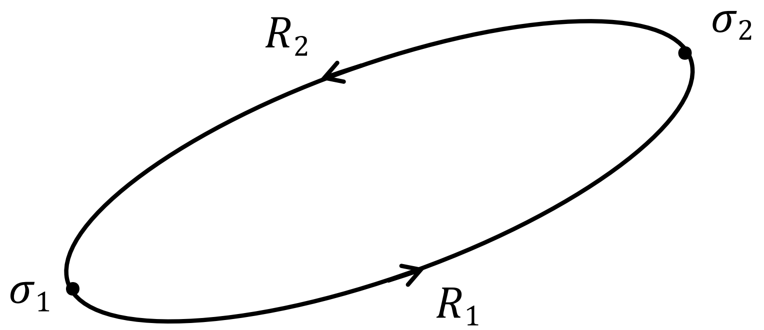
- *Thus*: $W = Q \leq 0$, or $\tilde{T}\sum_i \frac{\delta Q_i}{T_i} \leq 0$ or $\sum_i \frac{\delta Q_i}{T_i} \leq 0$

- *Hence*: $\boxed{\oint \frac{\delta Q}{T} \leq 0}$ 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 S_{TD}

- Consider a *reversible* cycle:



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

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

- <u>*Thus*</u>: $\displaystyle\underset{R_1}{\int_{\sigma_1}^{\sigma_2}} \frac{\delta Q_R}{T} = -\underset{R_2}{\int_{\sigma_2}^{\sigma_1}} \frac{\delta Q_R}{T} = \underset{R_2}{\int_{\sigma_1}^{\sigma_2}} \frac{\delta Q_R}{T}$

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

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

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

"thermodynamic entropy"

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

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

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.

For an *irreversible* process connecting equilibrium states σ_1 and σ_2, S_{TD} 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.

2. Only defined for *equilibrium states*.

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

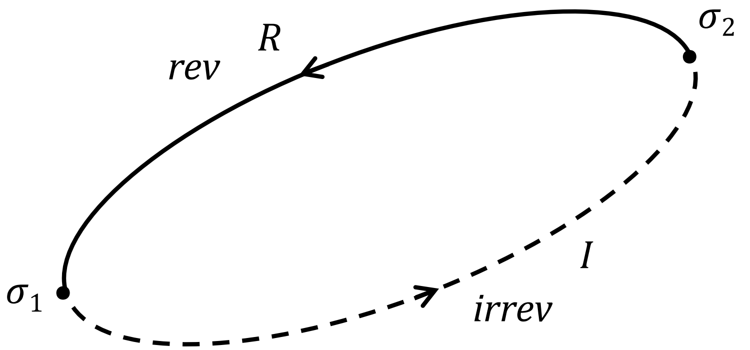
$$dS_{\text{TD}} = \delta Q_{\text{R}}/T$$

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

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

3. Principle of Increasing S_{TD}

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 $\displaystyle {}_I\!\int_{\sigma_1}^{\sigma_2} \frac{\delta Q}{T} + {}_R\!\int_{\sigma_2}^{\sigma_1} \frac{\delta Q_R}{T} < 0$ or $\displaystyle {}_I\!\int_{\sigma_1}^{\sigma_2} \frac{\delta Q}{T} - {}_R\!\int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T} < 0$

- *Thus*: $\displaystyle \Delta S_{\text{TD}} = {}_R\!\int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T} > {}_I\!\int_{\sigma_1}^{\sigma_2} \frac{\delta Q}{T}$ ←

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

- *So in general*: $\displaystyle \Delta S_{\text{TD}} = {}_R\!\int_{\sigma_1}^{\sigma_2} \frac{\delta Q_R}{T} \geq \int_{\sigma_1}^{\sigma_2} \frac{\delta Q}{T}$

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

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

The change in thermodynamic entropy for a thermally isolated irreversible process between equilibrium states increases, and is unaltered for a reversible process.

4. S_{TD} and the Approach to Equilibrium

- How does the *Principle of Increasing S_{TD}* relate to the *Equilibrium Principle*?

One way of formulating the 2nd Law!

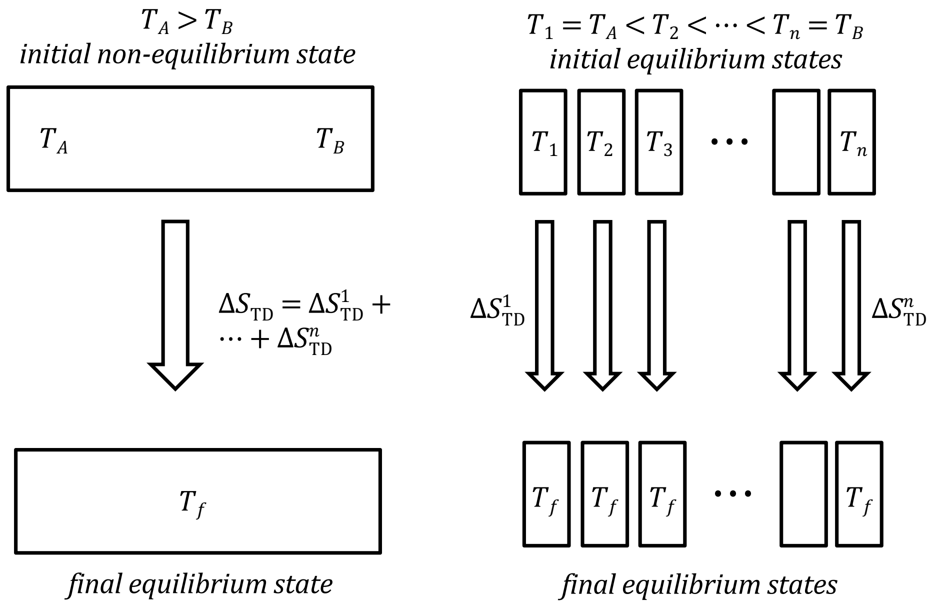
The Minus 1st Law!

- The "approach to equilbrium" is a process that connects a *non-equilibrium* state with an equilibrium state!

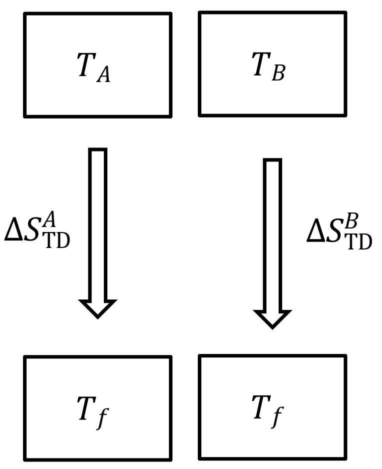
How is S_{TD} defined for such a process? And does it increase/remain unaltered?

General method:

- System in initial *non-equilibrium* state can be decomposed into subsystems, each in an initial *equilibrium* state.
- Process that takes system from initial non-equilibrium state to final equilibrium state can be decomposed into a sum of processes that take each subsystem from its initial equilibrium state to final equilibrium state.
- Each sub-process has well-defined change in S_{TD}, and sum of these (i.e., change in S_{TD} for entire system) cannot be negative!



Ex. System composed of subsystems A, B with initial temps T_A, T_B and heat capacities $C_A \equiv \delta Q_A/dT$, $C_B \equiv \delta Q_B/dT$ that are brought into contact and then allowed to reach equilibrium at temp T_f.



- System: initial *non-equilibrium* state σ_i, final *equilibrium* state σ_f.
- A, B: initial *equilibrium* states σ_i^A, σ_i^B, final *equilibrium* states σ_f^A, σ_f^B.
- Suppose σ_i^A, σ_f^A are connected by a reversible process, at each step of which A absorbs a small amount of heat $\delta Q_A = C_A dT$ from a reservoir resulting in an increase dT in temperature.
- Change in S_{TD} for A is:

$$\Delta S^A_{\mathrm{TD}} = S^A_{\mathrm{TD}}(\sigma_f^A) - S_A(\sigma_i^A) = \int_{\sigma_i^A}^{\sigma_f^A} \frac{\delta Q_A}{T} = \int_{T_A}^{T_f} \frac{C_A dT}{T} = C_A \ln\frac{T_f}{T_A}$$

Similarly for ΔS^B_{TD}

- Change in S_{TD} for entire system is:

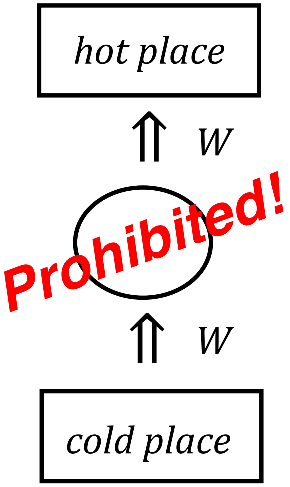
$$\Delta S^A_{\mathrm{TD}} + \Delta S^B_{\mathrm{TD}} = C_A \ln\frac{T_f}{T_A} + C_B \ln\frac{T_f}{T_B}$$

<u>Claim</u>: This expression cannot be negative!

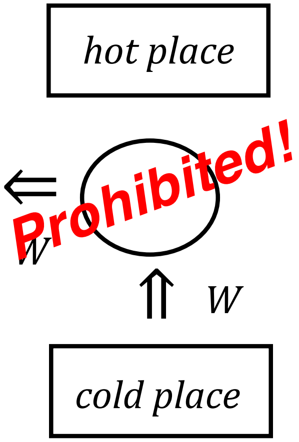
$$\begin{aligned} C_A \ln\tfrac{T_f}{T_A} + C_B \ln\tfrac{T_f}{T_B} &\geq C_A(1 - T_A/T_f) + C_B(1 - T_B/T_f) \quad \longleftarrow \ \ln y \geq 1 - 1/y \\ &= T_f^{-1}[C_A(T_f - T_A) + C_B(T_f - T_B)] \\ &= T_f^{-1}(Q_A + Q_B) \\ &= 0 \quad \longleftarrow \ \text{total work} = 0 \end{aligned}$$

5. Summary of 2nd Law of Thermodynamics

(1) *Clausius Form*: No cyclic process in which heat is transfered from cold to hot place without work input:



(2) *Thomson Form*: No cyclic process in which there is a conversion of heat to work without exhaust:



Consequence of 2nd Law:
The *thermodynamic entropy* S_{TD} of a thermally isolated irreversible process between equilibirum states increases, and is unalterted for a reversible process.

Absolute statements!

Meant to hold for any system subject to thermodynamical analysis.

Summary of Entailments

(2nd Law (Clausius Version))

There can be no cyclic process whose sole effect is the transfer of heat from a cold place to a hot place.

⇒

(Carnot's Claim #2)

In a reversible cyclic process, the work produced depends only on the temperature of the hot and cold places, and not on the working fluid.

⇒

(Clausius' Inequality)

In a cyclic process, the sum of all transformations $\delta Q/T$, consisting of an element of heat δQ absorbed by the system at temperature T, must be less than or equal to zero:

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

⇒

(2nd Law (Entropy Version))

The thermodynamic entropy of a thermally isolated system increases in any irreversible process and is unalterted in a reversible process:

$$\Delta S_{\mathrm{TD}} \geq 0$$

(2nd Law (Clausius Version))

⇕

(2nd Law (Thomson Version))

There can be no cyclic process whose sole effect is the extraction of heat from a source and the performance of an equivalent amount of heat.