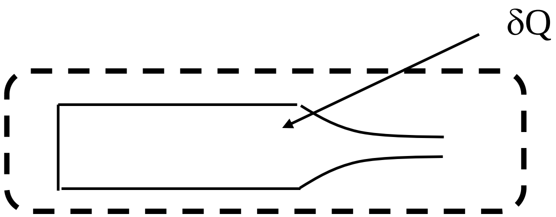
The Second Law of Thermodynamics

Key Concepts:
- Reversibility and Irreversibility
- Entropy & Entropy Production
- Idealized Reversible Engines

Chapter 2 - 2nd Law
Chapter 3 - Availability Analysis
Chapter 4 - Availability Analysis and Cycles

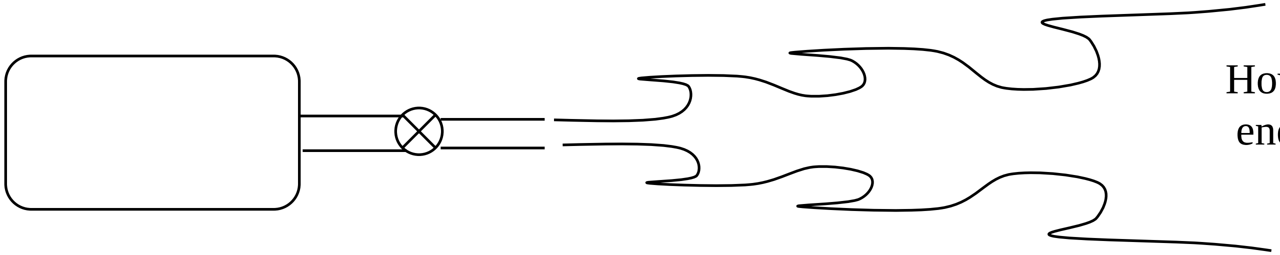
What are roles of 2nd Law Analysis:

1) Optimizing Performance for Cost



Question: At what temperature should heat be added (combustion) to maximize thrust?

2) Identifying large losses of availability energy



How much available energy is lost?

Our Approach for Studying the 2nd Law

- Statements about Reversible Engines

- Formulation of formal 2nd Law Statement

Development of 2nd Law for Closed Systems

Approach:

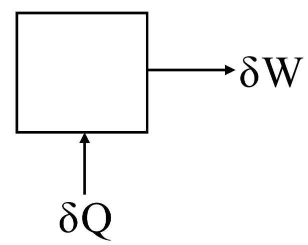
• Kelvin-Plank Statement

$$\oint \delta Q < 0 \quad ; \quad \oint \delta W < 0$$

Heat In   Work In

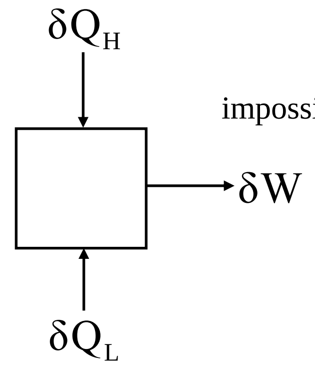
• Apply K-P to Heat Engine in Contact with One Reservoir

impossible



• Apply K-P to Heat Engine in Contact with Two Reservoirs

impossible



• Establish Thermodynamic Temperature Scale

• Apply K-P to Cycle in Contact with N-Reservoirs

$$\delta S = \frac{\delta Q_{REV}}{T}$$

$$P_S \text{ or } \sigma = dS - \frac{\delta Q}{T} \geq 0$$

Second Law for Closed Systems

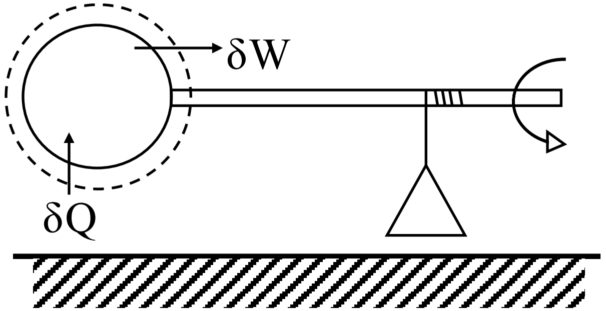
see Bejan pp.50-67, Wark 2.3-2.5

Cycle in Contact with One Heat Resevoir

Plank - “It is impossible to construct an engine that will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat reservoir.”

1st Law: $\delta Q - \delta W = dE$ (1)

$$\oint \delta Q = \oint \delta W \qquad (2)$$



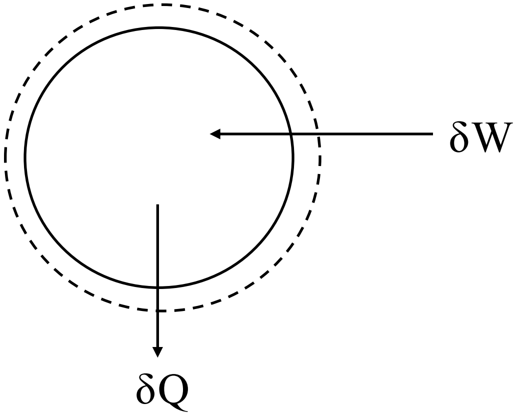
The impossibility of the process (based on experience) leads to:

$$\oint \delta W \le 0 \text{; net work into system} \qquad (3)$$

$$\oint \delta Q \le 0 \text{; net heat out of system} \qquad (4)$$

Based only on many attempted failures (Joule, Rumford…..)
This is called the “Kelvin-Plank” statement

Thus:



It is allowed to operate in a cycle, but not the reverse.

Questions for discussion:

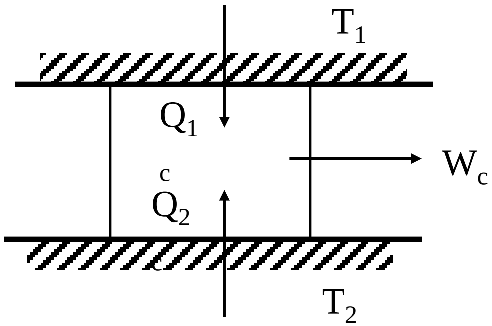
• Are (3) and (4) general? No, only for closed systems

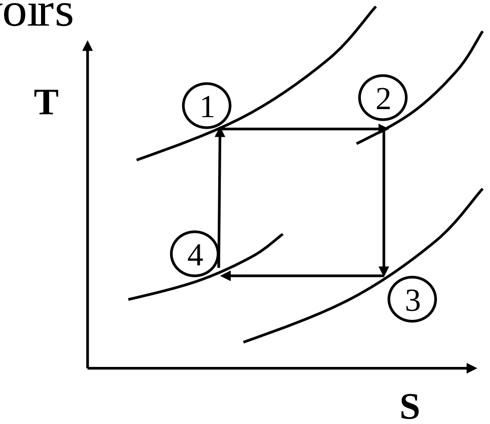
• Is this a formal proof? No, it is a statement based only on experience with many failures

Cycle in Contact with 2 Heat Reservoirs

Extend: $\oint \delta W \leq 0$ to two thermal reservoirs

<u>Carnot Engine</u>





Processes:

	1 to 2	constant temperature heat addition
	2 to 3	reversible, adiabatic expansion
	3 to 4	constant temperature heat rejection
	4 to 1	reversible, adiabatic compression

Assumptions:

- Each state is uniform T, P, V
- Every process is reversible

First Law: $Q_{1c} + Q_{2c} = W_c$

assume: $W_c > 0$

Then we have <u>three options</u>: on sign (direction) of Q

1) $Q_1 < 0$, $Q_2 < 0$ (both outflows)

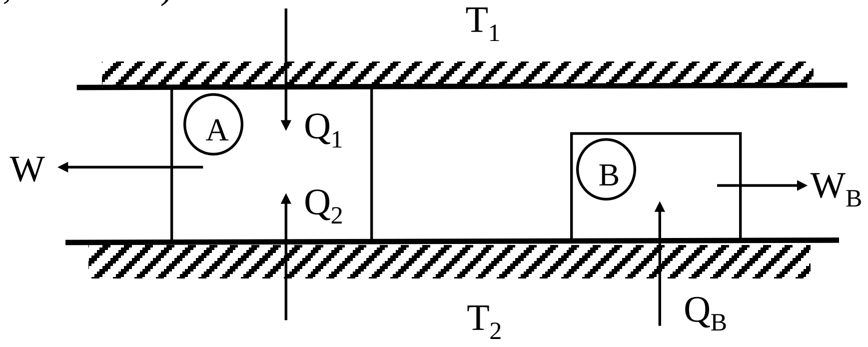
2) $Q_1 > 0$, $Q_2 > 0$ (both inflows)

2) $Q_1 Q_2 < 0$, i.e. Q_1, Q_2 are opposite sign

Option (1) - violates the 1st Law

Option (2) - $Q_1 > 0$ & $Q_2 > 0$ (both <u>inflows</u>)

This violates the 2nd Law Kelvin-Planck stattement as follows:
(see Bejan Fig 2.3, Wark 2-2)



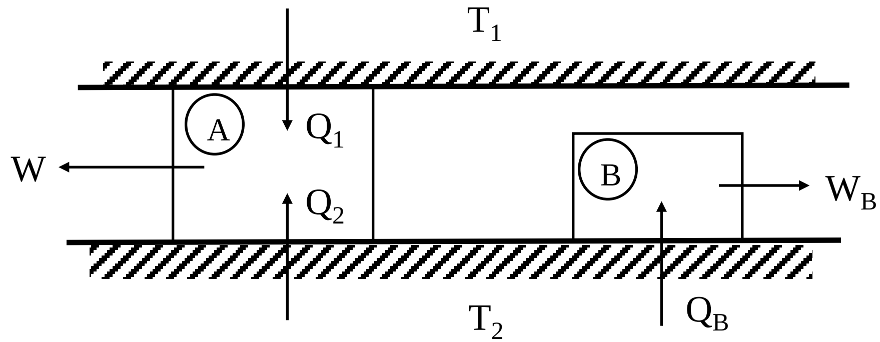
(i) At the completion of one cycle by system (A) we have the interactions:

$$W = Q_1 + Q_2 \qquad \text{for system (A)}$$

(ii) At this point we place system (B) in contact with the reservoir at T_2, and let it execute one cycle so that

$$Q_B = W_B$$

Note: $\Delta E_B = 0$ over one cycle



The Kelvin-Planck statement

for the single reservoir engine, forces $Q_B < 0$, i.e. an outflow from system (B)

(iii) Since the magnitude of Q_B was not specified, we simply allow:

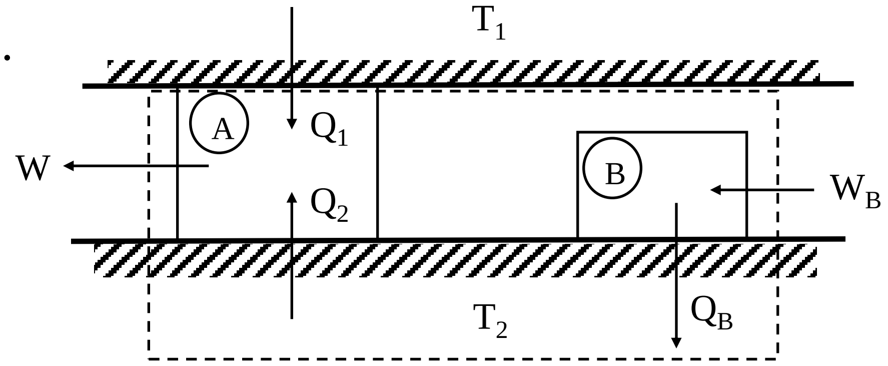
$$Q_B = -Q_2 \text{ (one cycle)}$$

(remember $Q_1 > 0$, $Q_2 > 0$, assumed inflows into (A) as one possible choice.

Then, for the reservoir

1st Law: $-Q_B - Q_2 = \Delta E = 0$ [no net change on reservoir]

Thus the reservoir also completes a cycle.



- And thus the composite system A, B, T_2 also completes a cycle.

So then: $Q_1 - W - (-W_B) = \Delta E_{A,B,2} = 0$

But, this cycle performed work ($W - W_B$) in contact only with the reservoir (T_1)
Therefore, the Kelvin-Planck statement requires:

$$(W - W_B) \le 0 \quad \text{(net work in)}$$

$$Q_1 \le 0 \quad \text{(heat out)}$$

But Q_1 was assumed to be > 0.

Case (ii) violates the 2nd Law!

Case (iii) - $Q_1 Q_2 < 0$ is the only option left!

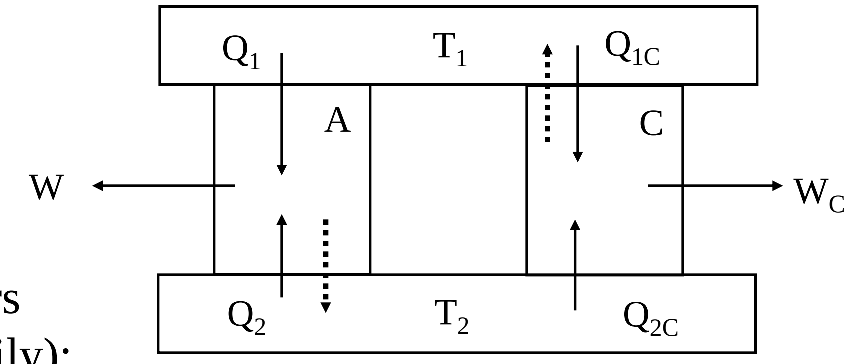
Case (iii) - $Q_1 Q_2 < 0$

i.e. Q_1 & Q_2 have opposite signs…...

Consider the situation:

- Let $Q_1 > 0$, i.e. inflow (positive)
  $Q_2 < 0$, i.e. outflow

Carnot Engine



Now attach a Carnot cycle to the reservoirs and size the Carnot cycle so that (arbitrarily):

- $Q_1 + Q_{1C} = 0$; $Q_{1C} = - Q_1$ (outflow from C)

So that T_1 reservoir also executes a cycle.

Since now A + C + Reservoir (1) execute a cycle while in contact only with reservoir (2) then:

Second Law:

$$\oint \delta W \leq 0 \; ; \text{(net work in)}$$

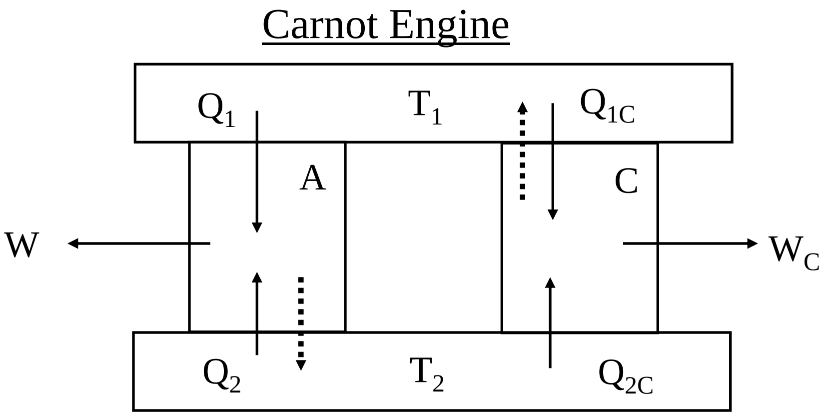
$$\oint \delta Q \leq 0 \; ; \text{(net heat out)}$$

We have the following: [W(in), net heat out]

$$Q_{1C} = - Q_1$$

$$\oint \delta Q = Q_2 + Q_{2C} \leq 0 \quad \text{(net heat outflow)}$$

- then $Q_{2C} \leq (-Q_2)$



Divide through by Q_1 (which is positive, assumed)
or by $(-Q_{1C}) = - (-Q_1) = + Q_1$ also positive

$$\text{then} \quad \frac{Q_{2C}}{(-Q_{1C})} \leq \frac{-Q_2}{(Q_1)}$$

Thus establishing a limit or ratio of heat transfer interactions. Re-write as:

$$\frac{-Q_2}{Q_1} \geq \left(\frac{Q_{2C}}{-Q_{1C}} \right)$$

The negative signs are there because of the heat engine sign convention.

To put in a simpler way:

$$\frac{|Q_{outflow}|}{|Q_{inflow}|} \geq \frac{|Q_{inflow, Carnot}|}{|Q_{outflow, Carnot}|}$$

The equality is for a <u>reversible</u> process

$$\left(\frac{|Q_{out, rev}|}{|Q_{in, rev}|}\right) = \frac{|Q_{in, Carnot}|}{|Q_{out, Carnot}|}$$

But we can see that our reversible case is just a <u>reversed Carnot cycle</u>; hence, our <u>reversible case</u> can serve as the limit for our 2-T engine, hence:

$$\frac{-Q_2}{Q_1} = \frac{|Q_{out}|}{|Q_{in}|} \geq \left(\frac{|Q_{out}|}{|Q_{in}|}\right)_{reversible}$$

And also: $W(= Q_{out} - Q_{in}) \geq W_{rev}(= Q_{out, rev} - Q_{in, rev})$

<u>Critical Question</u>

What is the limiting value of $\left(\frac{|Q_{out}|}{|Q_{in}|}\right)_{reversible}$?

Any reversible cycle

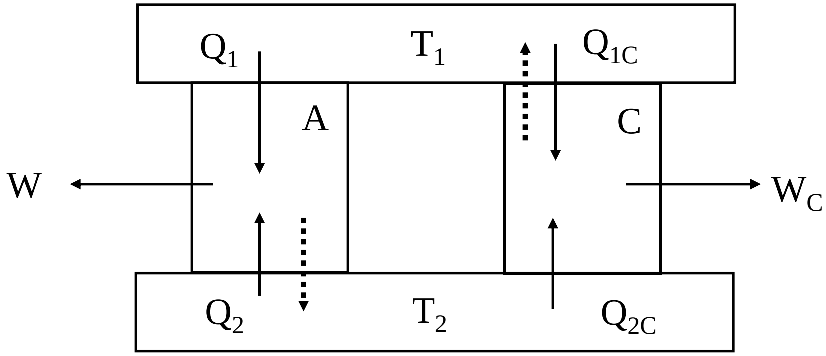
The Thermodynamic Temperature Scale

from last argument, we found:

$$\frac{-Q_2}{Q_1} \geq \left(\frac{-Q_2}{Q_1}\right)_{\text{reversible}}$$

$$\left(\frac{Q_{\text{outflow}}}{Q_{\text{inflow}}}\right) \geq \left(\frac{Q_{\text{outflow}}}{Q_{\text{inflow}}}\right)_{\text{reversible}}$$

Carnot Engine



- What did we initially specify about system A:
  - (1) it executes a cycle in contact with 2 reservoirs
  - (2) its state is always in equilibrium

- Nothing was said of the working fluid or the cycle

- What are the parameters left upon which $\left(\frac{-Q_2}{Q_1}\right)_{\text{rev}}$ may depend? What is its minimum value?

- Only T_1 and T_2

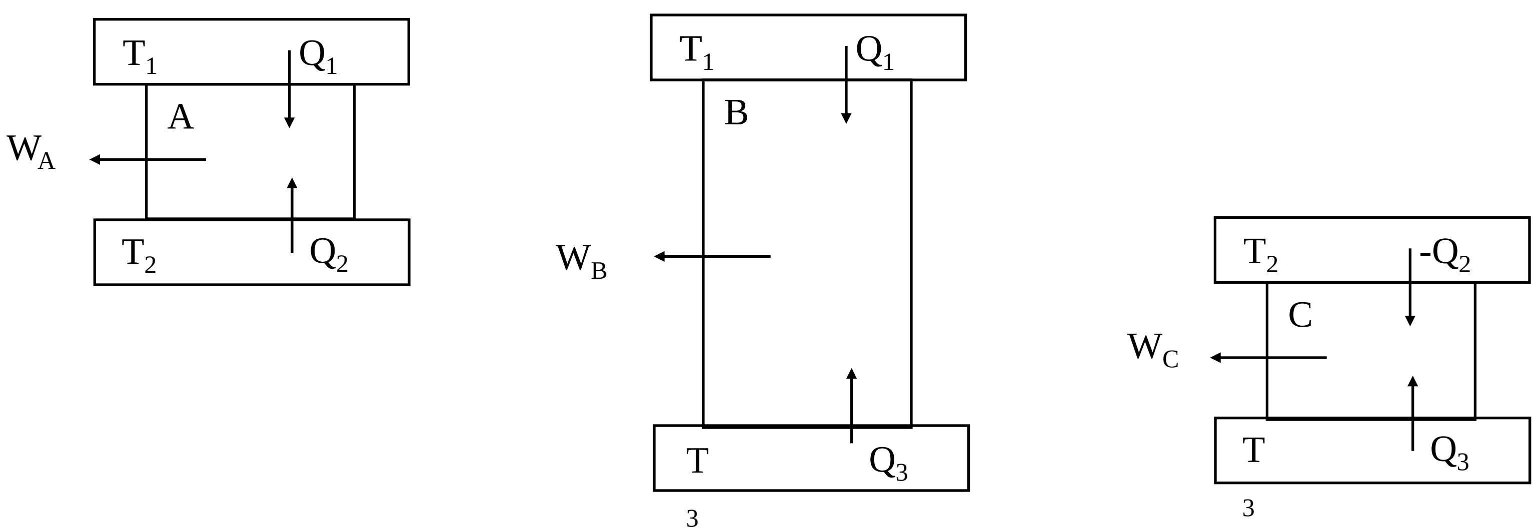
$$\frac{-Q_2}{Q_1} = f\,(T_1, T_2)$$

where the temperatures T_1, T_2 are read off of the same scale, yet to be established.

We can show:

$$\left(\frac{-Q_2}{Q_1}\right)_{rev} = \frac{\varphi(T_2)}{\varphi(T_1)}$$

as follows: Consider the reversible cycles:



(see Bejan, Fig. 2.4)...

For reservoir A: $\left(\frac{-Q_2}{Q_1}\right)_{rev} = f\,(T_1, T_2)$

reservoir B: $\left(\frac{-Q_3}{Q_1}\right)_{rev} = f\,(T_1, T_3)$

reservoir C: $\left(\frac{-Q_3}{-Q_2}\right)_{rev} = f\,(T_2, T_3)$ [why are there all the same function f (   )?]

Divide B by C:

$$\frac{\left(\frac{-Q_3}{Q_1}\right)_{rev}}{\left(\frac{-Q_3}{-Q_2}\right)_{rev}} = \frac{f\,(T_1, T_3)}{f\,(T_2, T_3)}; \quad \text{thus} \left(\frac{-Q_2}{Q_1}\right)_{rev} = \frac{f\,(T_1, T_3)}{f\,(T_2, T_3)}$$

But from A: $f\,(T_1, T_2) = \frac{f\,(T_1, T_3)}{f\,(T_2, T_3)}$

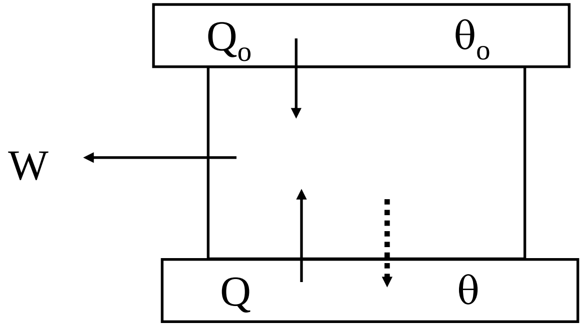
Thus since the left side does not depend on T_3, the analytical form of $f\,(T_1, T_2)$ is :

$$f\,(T_1, T_2) = \frac{\psi\,(T_1)}{\psi\,(T_2)}$$

Letting $\frac{1}{\psi} = \varphi$, then :

$$\left(\frac{-Q_2}{Q_1}\right)_{rev} = \frac{\varphi(T_2)}{\varphi(T_1)}$$

(reference termperature)



This marvelous idea is attributed to Kelvin.

Now let us be more specific about φ:

Let this be a reversible cycle that absorbs a unit of heat Q_o from a reservoir at a unit of temperature θ_o, and reject it to a reservoir at θ.

If one can perform an experiment to measure $\left(\frac{-Q}{Q_o}\right) = \frac{\varphi(T)}{\varphi(T_o)}$

for any reversible cycle running between θ and θ_o, one can find the functional form of $\varphi(\theta)$.

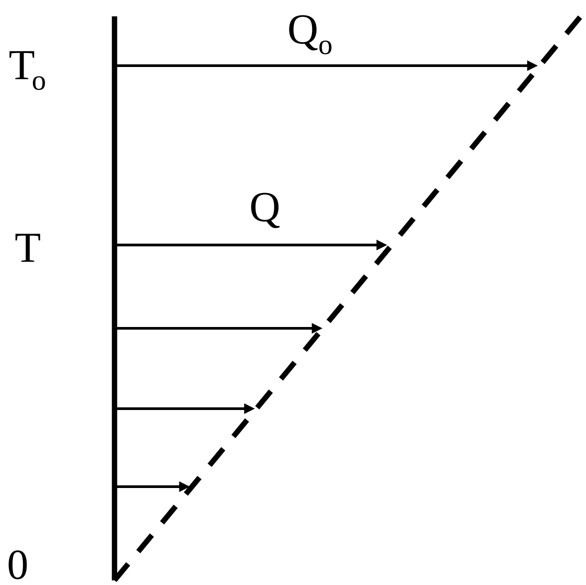
These numerical values of $\left(\frac{-Q}{Q_o}\right)_{rev}$ form the Thermodynamic Temperature Scale; from which we find:

the simplest form is:

$$\varphi \equiv T$$

$$\therefore\ T = T_o\left(\frac{-Q}{Q_o}\right)_{rev}$$

(See Bejan Fig. 2.5)



T_o=273.16°K

(Triple Point of water at 1atm P)

"Wedge of Minimum Q"

Now was it necessary to have chosen the <u>linear</u> function $\varphi \equiv T$?

Answer: No, any monotonic function would have sufficed because the T-sclae is free to be assigned.

The choice $\varphi \equiv T$ is traditional, seemingly because for an ideal gas as working fluid: $\varphi = T$

(Read Bejan pp. 60-61)

Finally, we obtain

$$\left(\frac{-Q_2}{Q_1}\right)_{rev} = \frac{T_2}{T_1} \qquad \text{or} \qquad \left(\frac{-Q_2}{Q_1}\right) \geq \left(\frac{-Q_2}{Q_1}\right)_{rev}$$

We can write:

$$\boxed{\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0}$$

Independence of sign of W assumed [Problem 2.2].

Or written in another form:

$$-\frac{Q_2}{T_2}-\frac{Q_1}{T_1}\geq 0$$

or:

$$\boxed{\frac{|Q_{outflow}|}{T_{outflow}}-\frac{|Q_{inflow}|}{T_{inflow}}\geq 0}$$

Cycle in contact with <u>2</u> reservoirs.

Second Law for a Cycle (in contact with any number of Thermal Energy Reservoirs)

(see Bejan, p. 61)

Per arguments in Bejan, for a cycle that is in contact with any number of Thermal Energy Reservoirs, and that produces work:

$$\sum_{i=1}^{n+1} \frac{Q_i}{T_i} \le 0$$

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

See Bejan proof ...

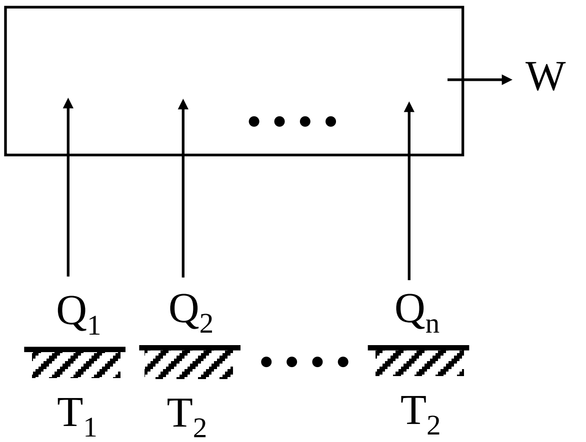


Figure 1

Where $\oint$ is the path integral over a closed path.

If the cycle is reversible: $$\oint \frac{\delta Q_{rev}}{T} = 0$$

Thus, if the "net change" in $\left(\frac{\delta Q_{rev}}{T}\right)$ is zero over a cycle, then $\left(\frac{\delta Q_{rev}}{T}\right)$ represents the change in a thermodynamic property called S. (Clausius, 1865)

Thus

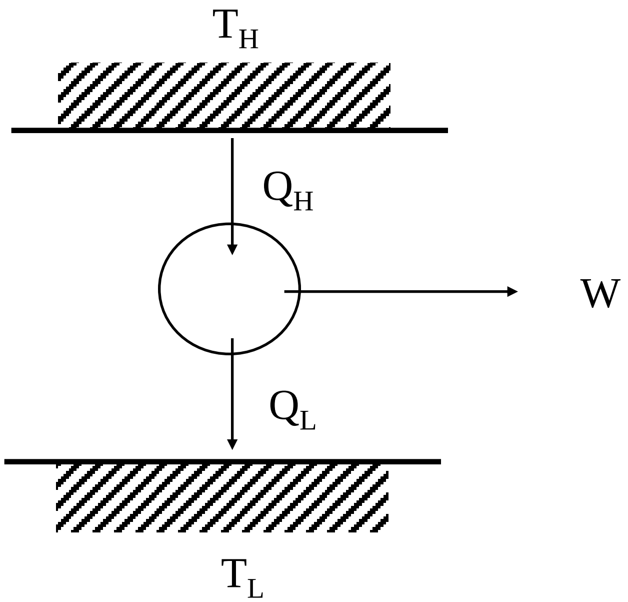
$$\boxed{dS \equiv \frac{\delta Q_{rev}}{T}}$$

<u>Defines</u> the property called <u>Entropy</u>!

and: $$S_2 - S_1 = \int_1^2 \frac{\delta Q_{rev}}{T}$$ over a process

<u>Example:</u>

Returning to the <u>2-T engine</u>:



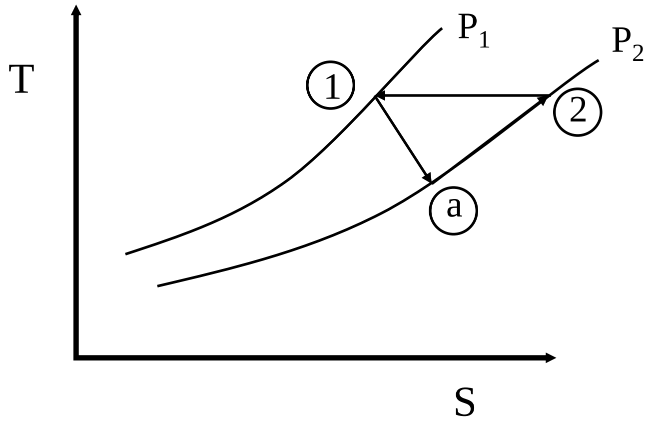
Since the cycle is <u>reversible</u>:

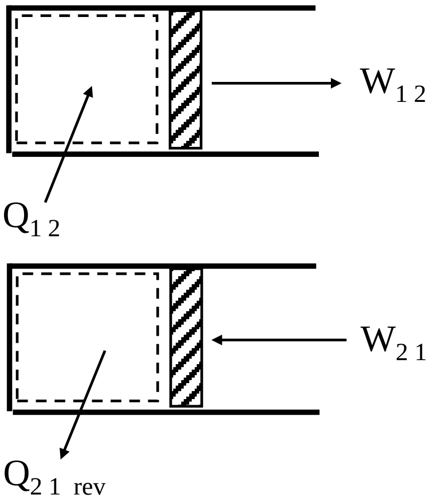
$$\oint \frac{\delta Q_{rev}}{T} = \oint \frac{\delta Q_H}{T_H} - \oint \frac{\delta Q_L}{T_L} = 0 \ !$$

$$\therefore \quad \frac{\delta Q_H}{T_H} = \frac{\delta Q_L}{T_L} \quad ; \quad \text{directly?}$$

Second Law for a Process:

Consider a process representation: as for example in Figure 1:





Process: ① → ⓐ Irreversible Expansion

ⓐ → ② Isobaric Heating

Process: ② → ① Reversible, Isothermal Compression

We can always find a reversible return path

We know for certain: $$\oint \frac{\delta Q}{T} \leq 0$$

$$\therefore \quad \int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q_{rev}}{T} \leq 0 \qquad \text{thus:} \quad \int_1^2 \frac{\delta Q}{T} \leq \int_1^2 \frac{\delta Q_{rev}}{T}$$

But: $\int_1^2 \frac{\delta Q_{rev}}{T} \equiv S_2 - S_1$ (by definition of the property S …..)

Thus: $\boxed{\int_1^2 \frac{\delta Q}{T} \leq S_2 - S_1}$

or introducing S_{gen}:

$$S_{gen} = \left\{ (S_2 - S_1) - \int_1^2 \frac{\delta Q}{T} \right\} \geq 0$$

Inflow, according to
heat engine convention…..

Implying that in the reversible process from ①⟶②, entropy was produced !

What's Important:

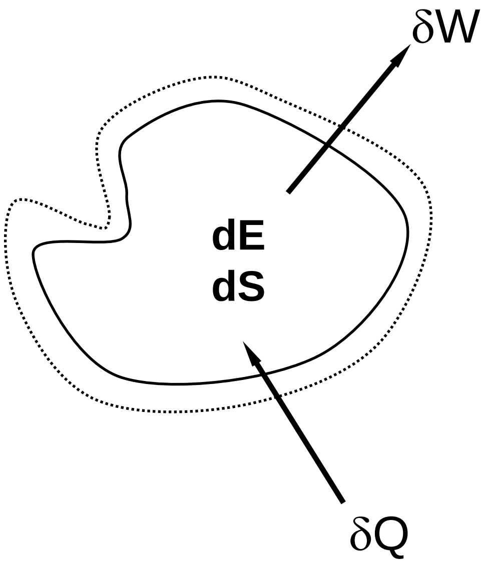
Cycle: $$\oint \frac{\delta Q}{T} \le 0$$ (in contact with any number of reservoirs)

Process: $$\int_1^2 \frac{\delta Q}{T} \le S_2 - S_1$$

definition: $$dS = \frac{\delta Q_{rev}}{T}$$

definition: $$S_{gen} = \left\{ \left(S_2 - S_1 \right) - \int_1^2 \frac{\delta Q}{T} \right\} \ge 0$$

Second Law for a C.M. (see Bejan, p. 64 Closed Systems)



For Internally Reversible Processes only:

$$dS = \frac{\delta Q_{rev}}{T} \qquad \left(S_2 - S_1\right) = \int_1^2 \frac{\delta Q_{rev}}{T}$$

For a process that is not Internally Reversible:

$$\left(S_2 - S_1\right) \geq \int_1^2 \frac{\delta Q}{T}$$

entropy change

entropy transfer; path dependent

The Strength of the Irreversibility is:

$$S_{gen} = \left\{\left(S_2 - S_1\right) - \int_1^2 \frac{\delta Q}{T}\right\} \geq 0$$

"S_{gen}" is the same as Reynolds & Perkins "P_s". It is path dependent!

“ T ” is understood to be the temperature of the system (C.S.) when the δQ is evaluated.

If T is uniform and constant:

$$S_{gen} = (S_2 - S_1) - \frac{Q_{1\,2}}{T} \geq 0$$

In the Reynolds & Perkins approach:

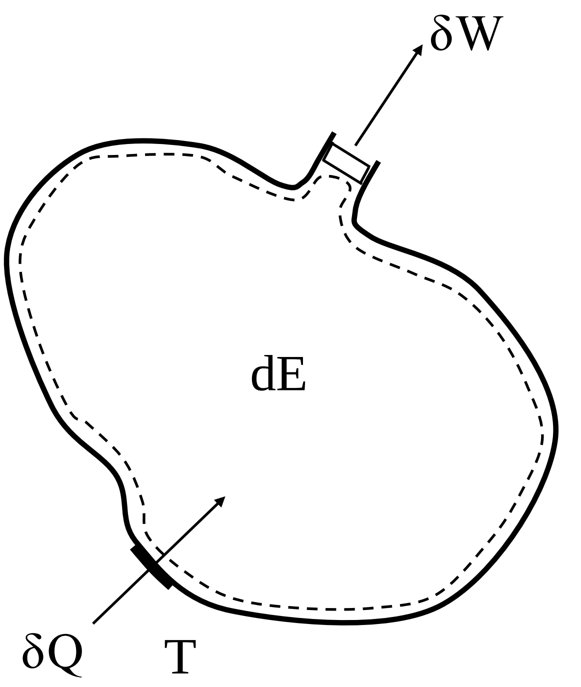
$$P_S = \Delta S + \left(\frac{Q}{T}\right)_{out} - \left(\frac{Q}{T}\right)_{in} \geq 0$$

In rate form:

$$\dot{P}_S = \frac{dS}{dt} + \left(\frac{\dot{Q}}{T}\right)_{out} - \left(\frac{\dot{Q}}{T}\right)_{in} \geq 0$$

The First <u>TdS</u> equation: <u>GIBBS EQUATION</u>

Consider a C.M. that has <u>one</u> reversible work mode, Pd**V**, undergoing a <u>process</u>: ① ⟶ ②



E.B. $\delta Q - \delta W = dE$

neglect P.E. $dE \to dU$

then: $\delta Q - \delta W = dU$

2nd Law: $\delta S - \dfrac{\delta Q}{T} \geq 0$

or $(S_2 - S_1) - \int_1^2 \dfrac{\delta Q}{T} \geq 0$

or $(S_2 - S_1) - \dfrac{Q_{1\,2}}{T} \geq 0$

Also: $\delta S_{gen} \equiv \left(dS - \dfrac{\delta Q}{T} \right) \geq 0$

$$TdS - \delta S_{gen} = \delta Q$$

then: $\quad TdS - \delta S_{gen} - \delta W = dU$

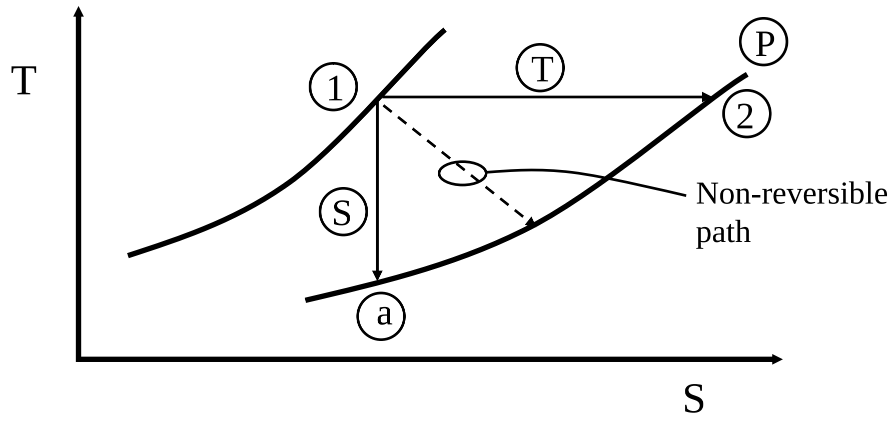
but: $\quad \delta W = PdV \quad$ thus:

$$\boxed{TdS - \delta S_{gen} = dU + PdV}$$

For a Reversible Process:

$$\delta S_{gen} = dS - \frac{\delta Q}{T} = 0$$

$$\therefore \quad \boxed{TdS = dU + PdV}$$



Equation applies to the change in state from ① ⟶ ② regardless of the path, reversible or not!

Ramifications of Gibbs Equation:

$$T ds = du + P dv$$

$$ds = \frac{du}{T} + \frac{P}{T} dv$$

$$\text{For ideal gas}: du = C_V dT \qquad \frac{P}{T} = \frac{R}{v}$$

$$ds = C_V \frac{dT}{T} + R \frac{dv}{v}$$

$$\boxed{s_2 - s_1 = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)}$$

Thus it is possible to express entropy change to other measurable thermodynamic properties.

Example

Carnot Engine

Example: Application of the Second Law to a Reversible Heat Engine

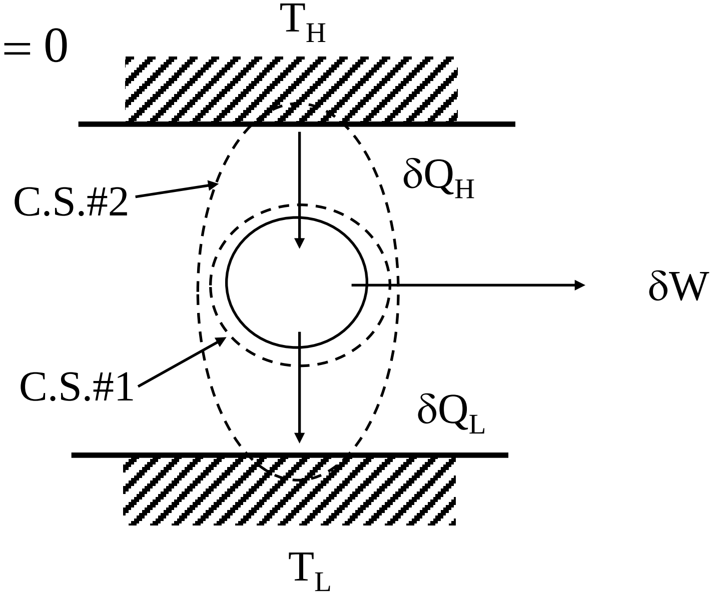
Consider the paradigm for a 2-T engine, the Carnot Engine:

We wish to analyze the deliverable work from a device of this type.

1st Law: C.S.#1

$$dE + (\delta Q_H - \delta Q_L) - \delta W = 0$$

Integrating: $(E_2 - E_1) + Q_{H\,1\,2} - Q_{L\,1\,2} - W_{1\,2} = 0$



2nd Law:

For an internally reversible process:

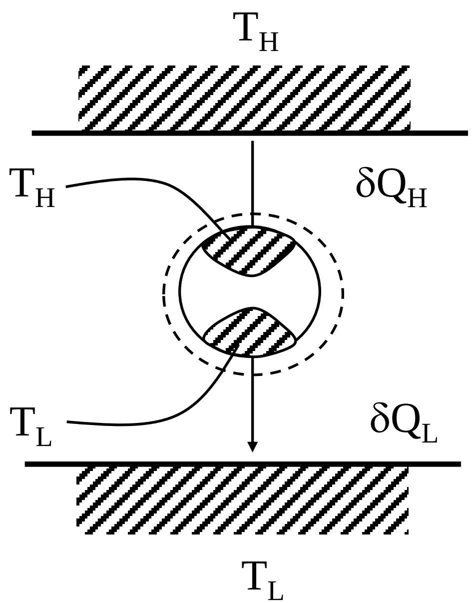
$$dS = \frac{\delta Q_{rev}}{T}$$

for C.S.#1

$$S_2 - S_1 = \int_1^2 \frac{\delta Q_{rev}}{T} = \int_1^2 \frac{\delta Q_H - \delta Q_L}{T}$$

If I choose C.S. #1, I do not know how to evaluate the integrals because I do not know T at position where δQ_H & δQ_L occurs. For example, if the engine operates at some fixed temperature, and we know it, then $T=T_{engine}$.

For the problem as shown, an easier way to resolve the issue is to use C.S. #2, or the following representation.



Then:

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q_H}{T_H} - \frac{\delta Q_L}{T_L} \right)$$

If T_H, T_L are fixed

$$S_2 - S_1 = \frac{\delta Q_{H1\,2}}{T_H} - \frac{\delta Q_{L1\,2}}{T_L}$$

If the system operate with no storage, or, if we consider that the state change (1 ⟶ 2) represents one cycle of a cyclic process, then:

$$E_2 - E_1 = 0$$

$$Q_{H1\,2} - Q_{L1\,2} = W_{1\,2}$$

$$S_2 - S_1 = 0 \qquad \Rightarrow \qquad \frac{\delta Q_{H1\,2}}{T_H} = \frac{\delta Q_{L1\,2}}{T_L}$$

$$W_{1\,2} = Q_{H1\,2} - Q_{L1\,2}\frac{T_L}{T_H} \qquad \Rightarrow \qquad \left\{ W_{1\,2} = Q_{H1\,2}\left(1 - \frac{T_L}{T_H}\right) \right\}$$

Writing in a different way:

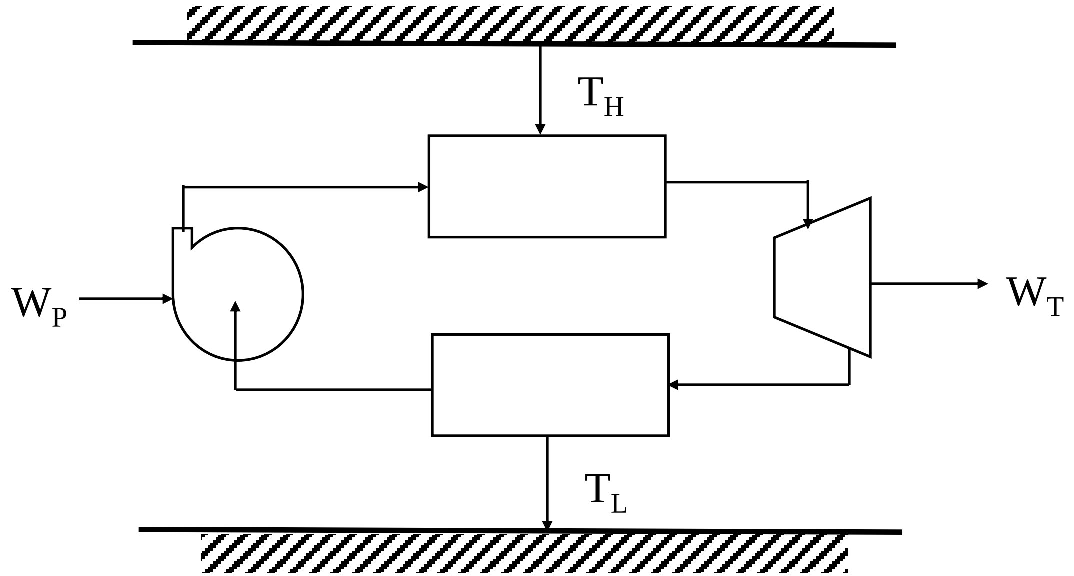
$$\eta_{carnot} = \frac{W_{12}}{Q_{12}} = \left(1 - \frac{T_L}{T_H}\right)$$

$$\text{If } T_L = T_H \qquad W_{1\,2} = Q_{1\,2} = 0$$

$$\text{If } T_L >> T_H \qquad W_{1\,2} \rightarrow Q_{1\,2}$$

What are the ramifications?

• In building steam engines / plants, the 2-T engine paradigm is obviously very important.



• The most important lesson:

- you can never recover all of the energy input (2nd Law)

- the conversion efficiency improves as $\frac{T_H}{T_L} >> 1$