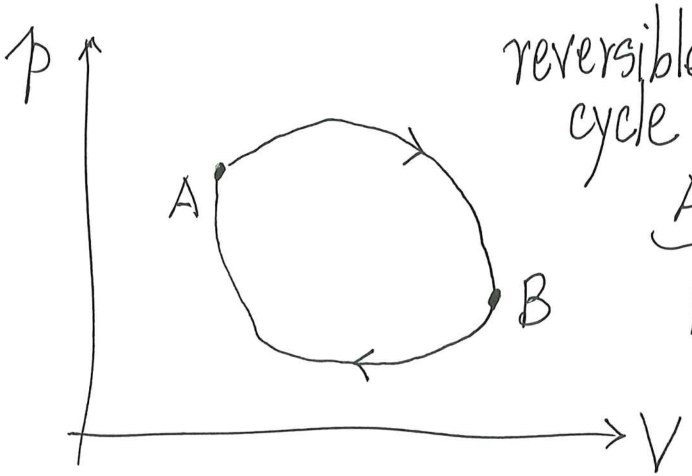
IV. The Second Law of Thermodynamics

A. Cycles

- Processes that take a system from an equilibrium state through many intermediate states (may be all equilibrium, may be not) and eventually back to the beginning equilibrium state. This constituents ONE CYCLE.

Reversible Cycles

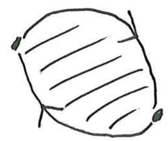
- Cycle that has all the processes being reversible, thus go through equilibrium states as intermediate states
- Can draw reversible cycle on indicator diagram
- No change in state functions / state variables after a cycle



reversible cycle

$$\underbrace{A \to B \to}_{\text{1 cycle}} \underbrace{A \to B}_{\text{another cycle}}$$

U_A goes back to the same U_A after a cycle [also $P_A \to P_B \to P_A$ (same), $T_A \to T_B \to T_A$ (same), $V_A \to V_B \to V_A$ (same),]

But $W_{\text{by system in 1 cycle}}$ = Area enclosed by  $\ne 0$

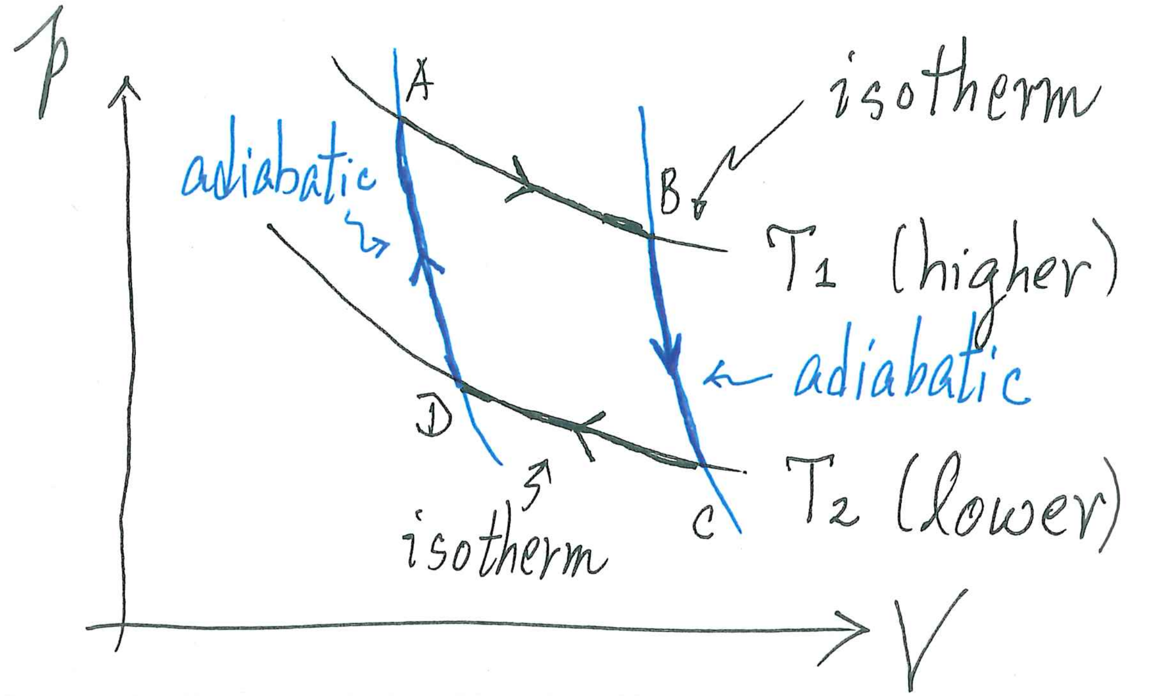
$$= \oint_{\text{cycle}} p\, dV$$

depends on details (paths) of cycle

1st law (consider 1 cycle)

$\underbrace{\Delta U = 0 \text{ (back to same state A)}}_{\text{so are other state functions}}$, $W \neq 0 \Rightarrow \underbrace{Q \neq 0}_{\text{some heat goes in}}$

B. The Carnot Cycle : It is a REVERIBLE CYCLE



a cycle

A → B → C → D → A

A → B	B → C	C → D	D → A
isothermal expansion	adiabatic expansion	isothermal compression	adiabatic compression
$W_{by\ system}$	$W_{by\ system}$	$W_{on\ system}$	$W_{on\ system}$
$Q_{into\ system}$	$Q = 0$	$Q_{out\ of\ system}$	$Q = 0$

Total $W_{by\ system}$ in 1 cycle =  $\neq 0$

Area

Back to A in 1 cycle $\Rightarrow \Delta U = 0$

Net $\Delta Q_{in\ 1\ cycle} = Q_{into\ system} - Q_{out\ of\ system}$

1st law $0 = \Delta Q_{in\ 1\ cycle} - W_{by\ system\ in\ 1\ cycle}$

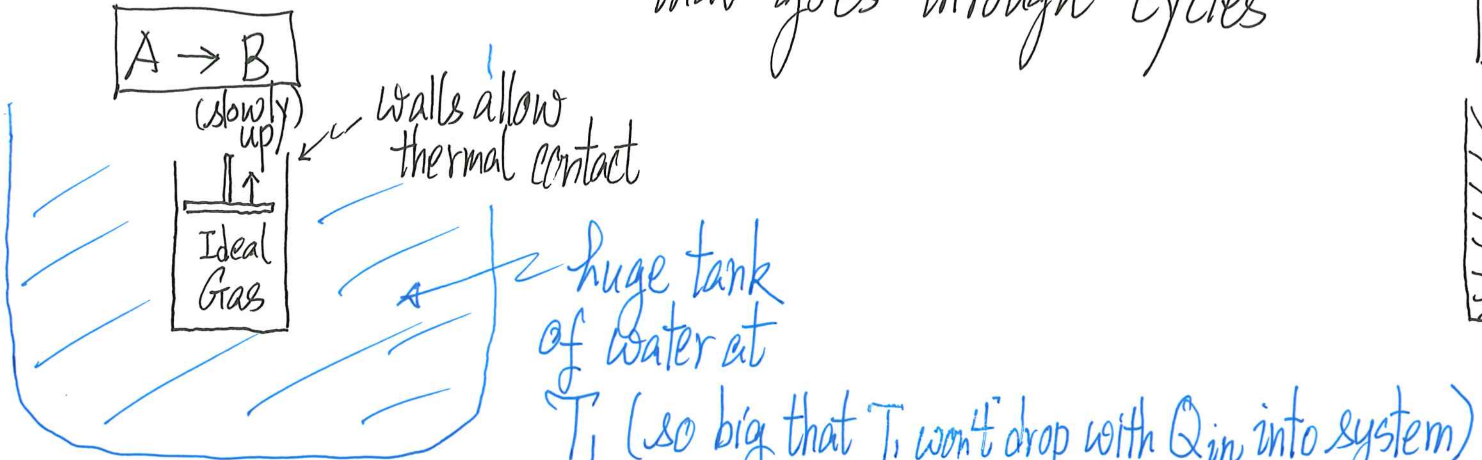
$$\Rightarrow \boxed{W_{by\ system\ in\ 1\ cycle} = \Delta Q_{into\ system\ in\ 1\ cycle}}$$

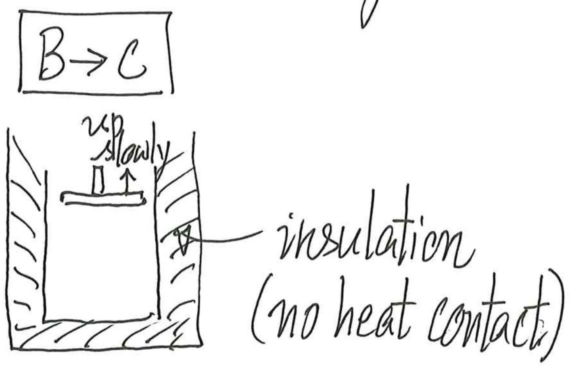
(argument true for any reversible cycle)

∴ In 1 cycle, the system takes in some heat Q_{in}, does some work $W_{by\ system}$, and rejects some heat $Q_{out\ of\ system}$. [Then system is back to A, and starts over again.]

It is working like <u>AN ENGINE</u>† (Carnot Engine).

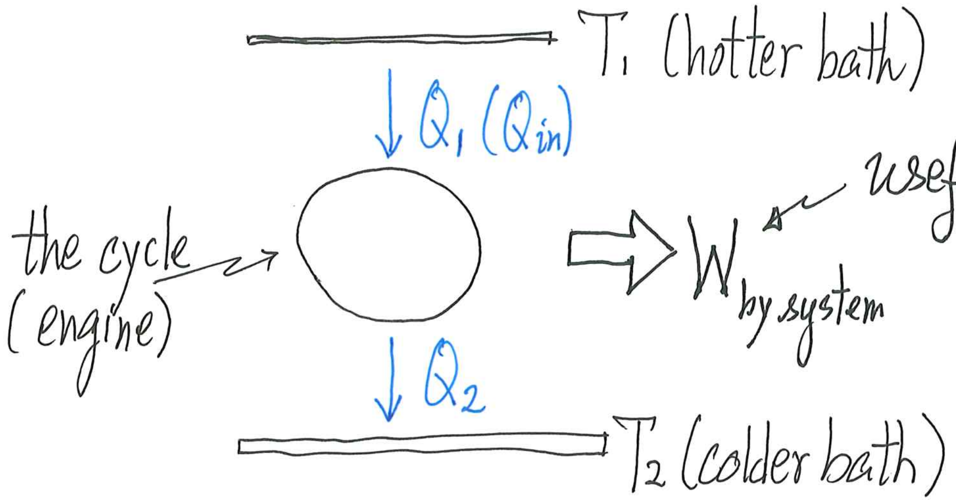
Carnot Cycle: Consider "<u>ideal gas</u> in cyclinder-piston" as our system that goes through cycles





† Any reversible cycle works as an engine, not only the one with isotherms & adiabatics under consideration.

Effectively, the Carnot Cycle is an engine that operates between two heat baths (reservoirs) [Carnot: involved only two heat baths]



"Heat Engines"

1st law ($\Delta U = 0$, cycle)

$W_{by\ system} = Q_1 - Q_2 =$ Net heat into system per cycle

(just energy conservation)

Engineering viewpoint

$$\boxed{\eta = \text{efficiency} = \frac{W_{by\ system}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}} \quad (1)$$

(still general)

make sense! How much of the taking in Q_1 is converted into useful $W_{by\ system}$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

Q_2 ← heat out (at T_2) [~ wasted energy]

Q_1 ← heat in (at T_1)

[Only if $Q_2 = 0$ [no wasted energy and no need to have bath at T_2], $\eta = 1$]

<u>Carnot:</u> Could η be 1?

How large can η be?

He found that his Carnot engine is the <u>MOST EFFICIENT</u>, even so η is bounded by a limit, and <u>ALL REVERSIBLE CYCLES</u> (any design, any material running in system) ARE as efficient as his Carnot engine.

This is effectively a way of stating the 2nd Law of Thermodynamics

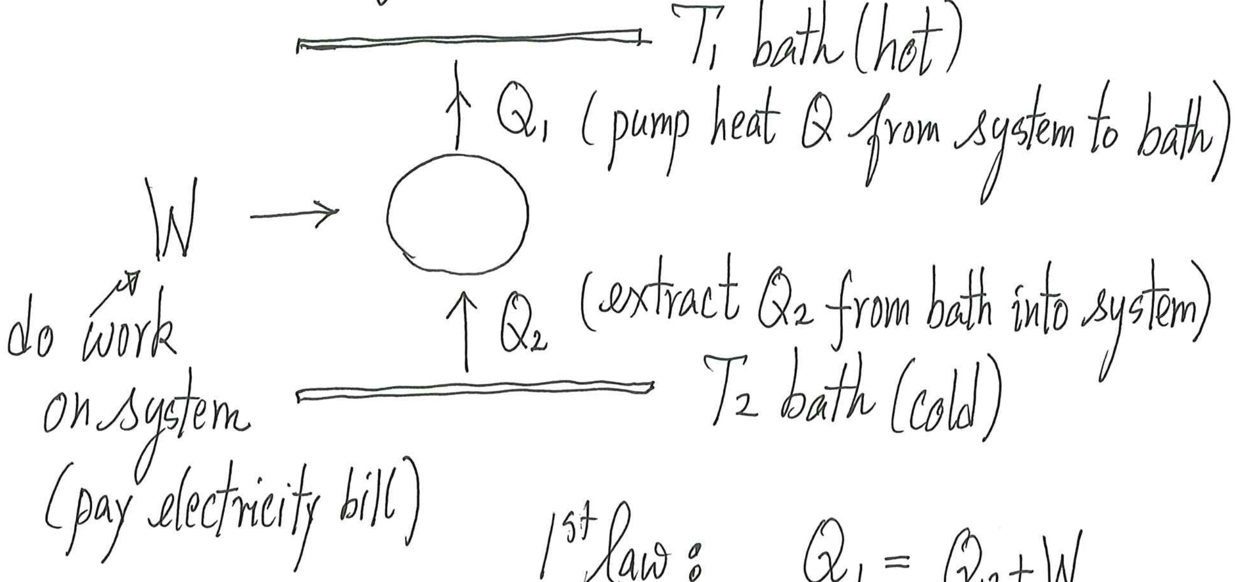
Remarks: "General" Carnot Cycle/Engine

- Historically, Carnot Engine
  - → reversible
  - → two isotherms and two adiabatic curves
  - → thus operates between TWO heat baths (T_1 & T_2)
  - → No need to refer to ideal gas as the working substance

- We used ideal gas here for its simplicity and there are existing results that we can use/copy
- The results turns out to be "no loss of generality" for reversible engines!

  a bit surprising!

Refrigerator



1st law: $Q_1 = Q_2 + W$

For refrigerators,

$$\eta^{\dagger}_{\text{refrigerator}} = \frac{Q_2}{W}$$

how much heat the work W can take out from a colder place?

a different practical viewpoint

It is a Carnot engine driven backwords!

[Thus ○ as refrigerator]

It is reversible.

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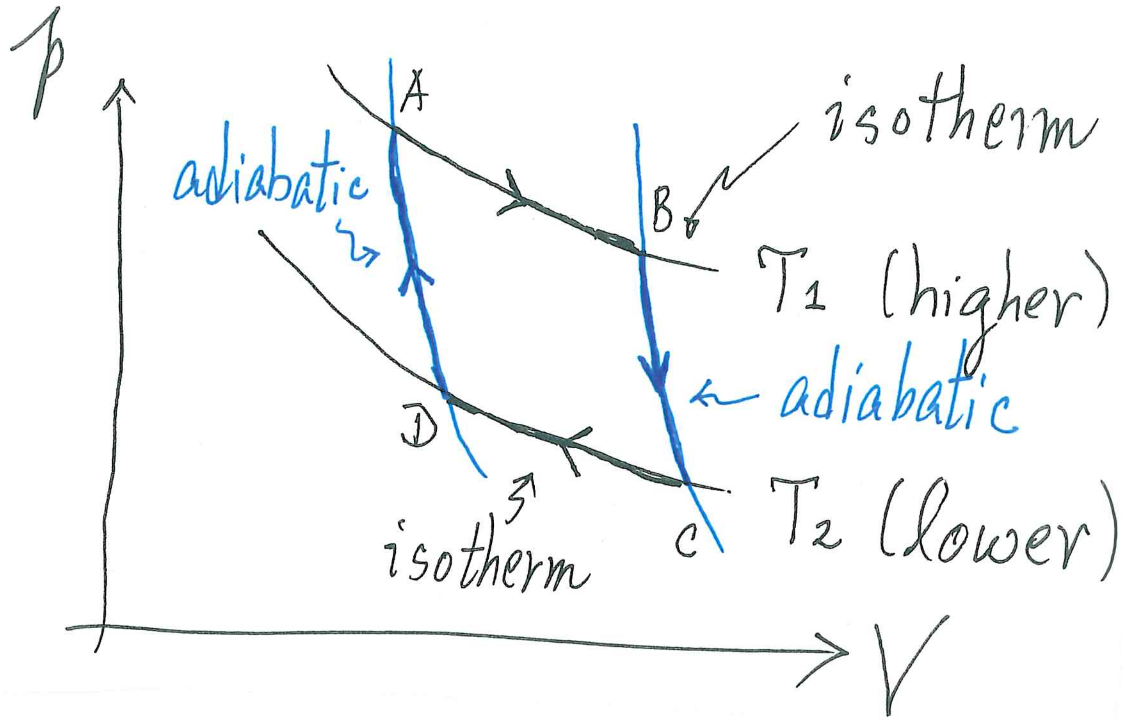
† $\eta_{\text{refrigerator}}$ is defined in the viewpoint of taking Q OUT OF A COLDER PLACE (engineering/functional viewpoint)
It is η in Eq.(1) that plays central role in building up the idea of entropy (2nd law)

C. Efficiency of Carnot Engine



(i) $A \to B$ isothermal expansion[+]

$$W_{\text{by system}} = RT_1 \ln\left(\frac{V_B}{V_A}\right)$$

$$Q_1 = RT_1 \ln\left(\frac{V_B}{V_A}\right)$$ Heat into system (>0)

(iii) $C \to D$ isothermal compression

$$W_{\text{on system}} = RT_2 \ln\left(\frac{V_C}{V_D}\right)$$

Q_2 = Heat reject by system

$$= RT_2 \ln\left(\frac{V_C}{V_D}\right) \quad (>0 \because V_C > V_D)$$

<u>Recall</u>: $\eta = 1 - \dfrac{Q_2}{Q_1}$

$$\therefore \eta = 1 - \frac{T_2}{T_1}\,\frac{\ln\left(\frac{V_C}{V_D}\right)}{\ln\left(\frac{V_B}{V_A}\right)}$$

almost there!

(not done yet!)

[+] <u>1 mole</u> of ideal gas in system. Otherwise $W = nRT\ln\left(\frac{V_B}{V_A}\right)$.
(# moles)

$B \to C$ adiabatic process $\Rightarrow T_B^{\frac{C_V}{R}} V_B = T_C^{\frac{C_V}{R}} V_C \Rightarrow T_1^{\frac{C_V}{R}} V_B = T_2^{C_V/R} V_C$

$D \to A$ adiabatic process $\Rightarrow T_D^{\frac{C_V}{R}} V_D = T_A^{C_V/R} V_A \Rightarrow T_2^{\frac{C_V}{R}} V_D = T_1^{C_V/R} V_A$

$$\therefore \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Carnot (1824)

$$\therefore \quad \boxed{\eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1}} \quad (2)$$

A most important result / and simplest in thermodynamics!

- fixed by T_1, T_2 of hotter and colder baths
- No reference to the materials (here ideal gas)
- As simple as it can be [given an engine (reversible) operating between T_1 & T_2]
- Must recall it is about <u>reversible</u> cycle
- Not obvious that η_{Carnot} is the best one can do (theoretical maximum)!

D. Why do we need the second law

1st law : Just conservation of energy

start with (a metal bar)

(wait → system approaches equilibrium)

(daily life experience : this happens!)

But start with

(daily life experience : this does NOT happen)

Energy Conservation viewpoint : Nothing Wrong (1st law OK)

But it just doesn't happen! [Need a law saying that this can't happen!]

Many such one-sided phenomena (naturally irreversible phenomena)

- Broken glass (pieces won't come back to form the glass)
- Died down swinging pendulum won't start swinging again

Arrow of time ??

(despite microscopic rules don't distinguish time moving forward or backward)

<u>What to do then?</u>

- Physicists are very practical!
- Just "say that such phenomena" can't happen & make it a law!
- So many "laws"? This & that can't happen!
- We are better than that! Hopefully, <u>one statement</u> can ban all the phenomena that we don't see them happening!

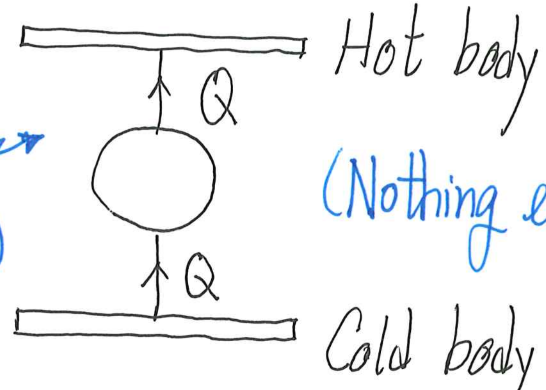
E. The Second Law of Thermodynamics

- There are several statements of the Law
- Clausius Statement (~1850) of 2nd Law

> It is impossible to construct a device [meaning an engine] that, operating in a cycle, produces no other effect [also as "whose sole effect"] than the transfer of heat from a cooler body to a hotter body.

Pictorially,

NOT ALLOWED



(Nothing else, no need to invoke W, "free of charge")

The device is working as a refrigerator.

So it bans | Cold Hot | $\xrightarrow{\text{time goes by}}$ | Colder Hotter |

(banned from happening)

[Why? Because it doesn't happen!]

The Law describes how Nature works! (Can't derive it!)

To proceed, we must take a form of 2nd Law as the truth[+].

Consequences

Carnot Engine is the most efficient for Engines operating between two baths

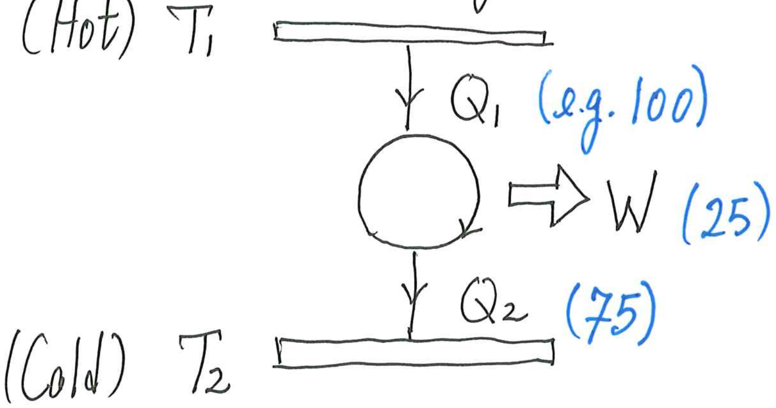
- Key point in argument: Carnot Engine is a reversible engine

can run backward as refrigerator

[+] Based on experiments and observations. There are other statements.

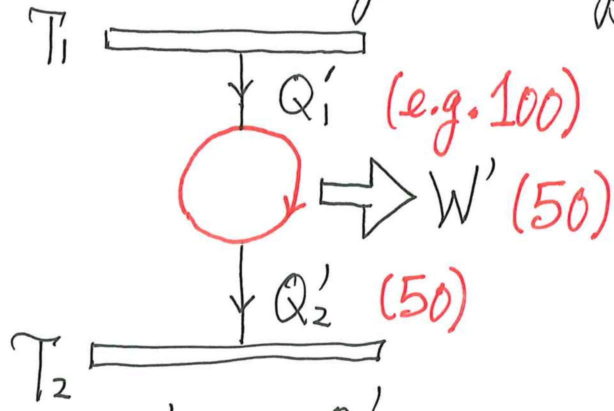
Let there be a hypothetical engine <u>more efficient</u> than Carnot engine

e.g. Carnot Engine



$$\text{e.g. } \eta = 1 - \frac{Q_2}{Q_1} = 0.25$$

Someone's claim of a More Efficient Engine



$$\eta' = 1 - \frac{Q_2'}{Q_1'} = 0.5 \text{ (better one!)}$$

(i) Recall: We had Q_1 and Q_2

$$W_{1\,cycle} = Q_1 - Q_2 \quad (1^{st} \text{ law})$$

$$= RT_1 \ln\left(\frac{V_B}{V_A}\right) - RT_2 \ln\left(\frac{V_C}{V_D}\right) \quad (1 \text{ mole})$$

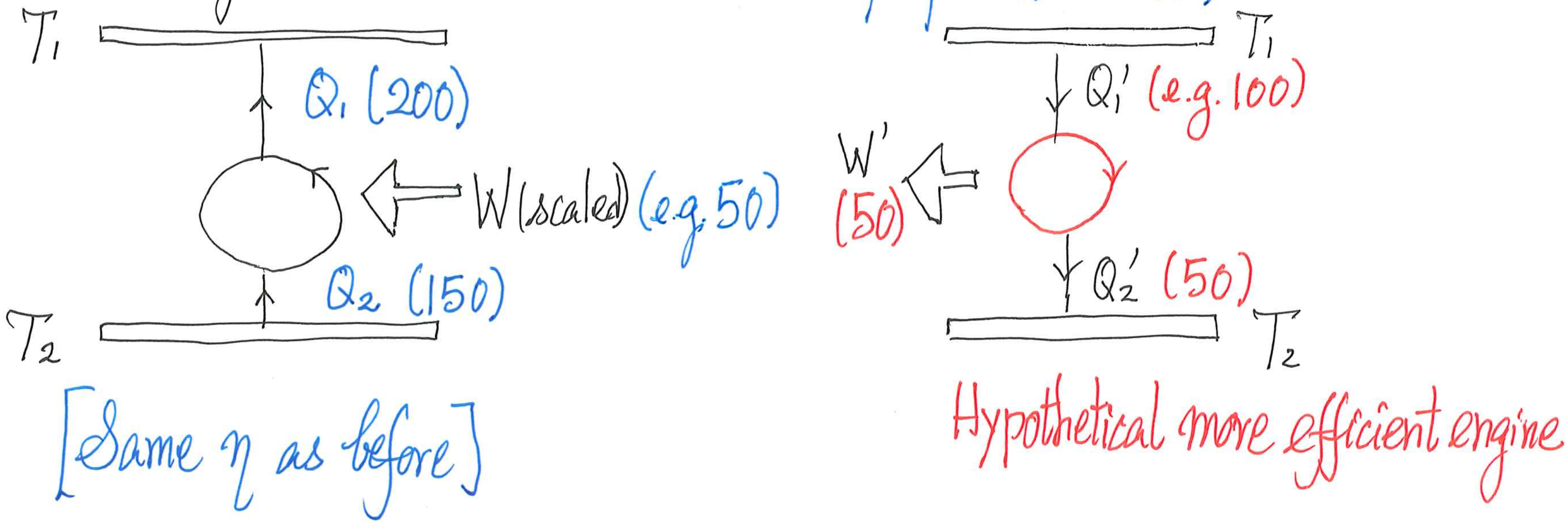
$$= R(T_1 - T_2) \ln\left(\frac{V_B}{V_A}\right) \quad (1 \text{ mole})$$

<u>Key Point</u>: Can scale size [n moles] to get a target $W_{1\,cycle}$

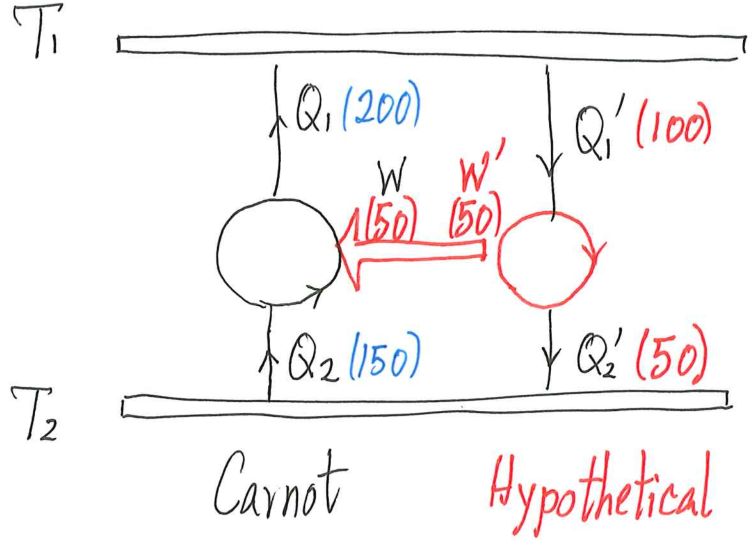
(ii) Scale size to make use of the W' from the hypothetical energy

(iii) Carnot engine can be run backwards as a refrigerator (reversible)

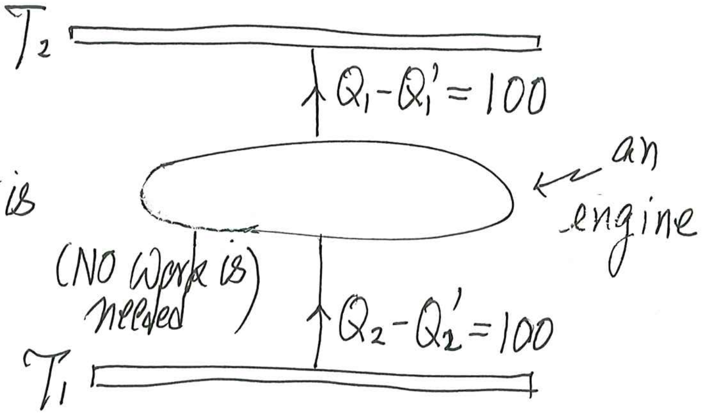
Carnot engine run backwards (scaled to prepare to use W')



(iv) Put them together and form a (composite) engine



NET Result is



Banned by 2nd Law! → This is an engine operating in a cycle whose sole effect is to transfer heat from a colder to a hotter body!

∴ The suggestion of an engine more efficient than the Carnot engine operating between T_1 and T_2 <u>violates</u> the 2nd law

(3) $\boxed{\eta_{Carnot} = 1 - \dfrac{T_2}{T_1} \text{ is the highest efficiency of an engine operating between } T_1 \text{ and } T_2}$

<u>Carnot's Theorem</u>

All reversible engines are equally efficient[†]: Corollary to Carnot's Theorem

Meaning: all designs (must be reversible)

Not necessary running on ideal gas, but any substance!

can run backwards

$$\boxed{\eta = 1 - \frac{T_2}{T_1} \equiv \eta_{rev}}$$

emphasizes ALL reversible engines are equally efficient

Why? Do it yourself!

e.g. If there is a hypothetical reversible engine that is MORE (OR LESS) efficient than Carnot engine, then connect it with Carnot Engine, the Composite engine will do things that violate the 2nd law.

Try it! Similar to what we just did.

† **Pay attention: This is a breakthrough in Science and in physics**

- We started with ideal gas as the working substance,

  but $\eta_{rev} = 1 - \dfrac{T_2}{T_1}$ is general for reversible engines operating between two baths T_1 (hot) and T_2 (cold)

  [an example of going from special to general cases without effort]

  （「以偏概全」而且结论是正确的！）

  The root of the success is the <u>reversibility</u> of the engine.

Something BIG follows...

$$\underbrace{\eta_{\text{irreversible}}}\ <\ \eta_{\text{rev}} \qquad \text{(logic)}$$

e.g. part of cycle involves states out of equilibrium

There is an inequality entering Thermodynamics!

This inequality (and its generality) propagates into other inequalities in thermodynamics, e.g

$$dS \geq 0 \quad [\text{isolated systems, } \underbrace{dS > 0 \text{ naturally happens}}_{\text{Yet another statement of 2nd Law}}]$$

To be Fair... Historical Remarks

- Carnot Engine: Reversible and two heat baths (θ_1 and θ_2)
- $\eta = 1 - \dfrac{Q_2}{Q_1}$ found (argued) to be the same for all reversible engines operating between two baths (not related to details, e.g. working substance)

$$\Rightarrow \frac{Q_2}{Q_1} = \mathcal{F}(\theta_1, \theta_2) \qquad \text{same function of } \theta_1, \theta_2$$

Using this universality to define the thermodynamic (absolute) temperature scale, i.e.

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

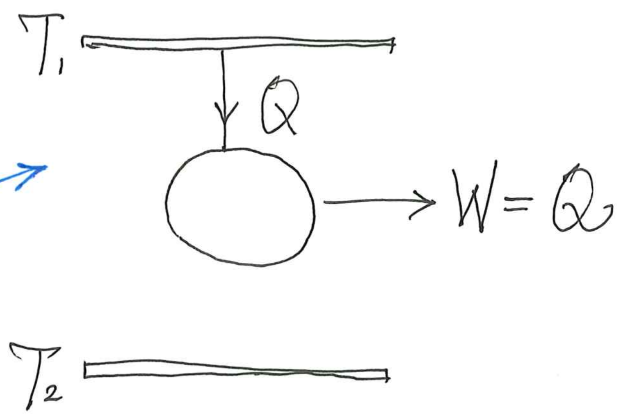
Then established that the thermodynamic temperature (T) (needs no reference to substance) is equivalent to the ideal gas temperature scale (θ) (relying on $pV = nk\theta$).

F. Kelvin-Planck statement of 2nd Law

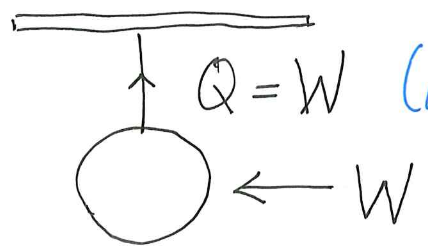
It is impossible to construct a device that, operating in a cycle, will produce no other effect than extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work. [It is about heat to work 100% in a cycle]

Pictorially,

NOT ALLOWED



But

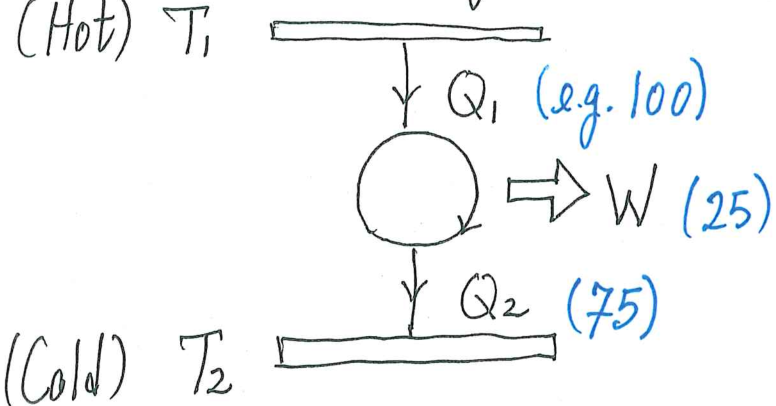


is OK (c.f. Joule's experiment)

Ex.: Show Clausius Statement and Kelvin-Planck statement are one implying the other [OR violating K-P implies violating Clausius]

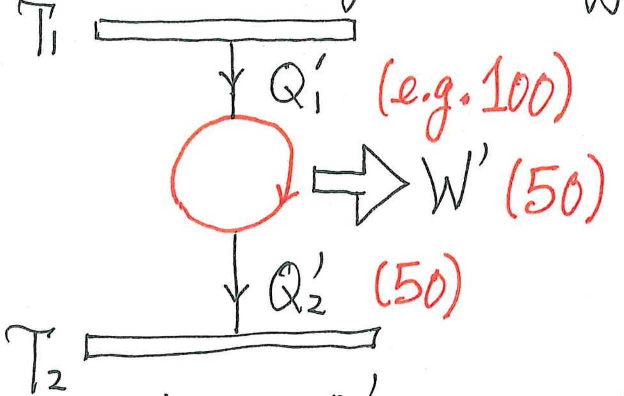
Claiming a more efficient engine exists also violates Kelvin-Planck statement

e.g. Carnot Engine



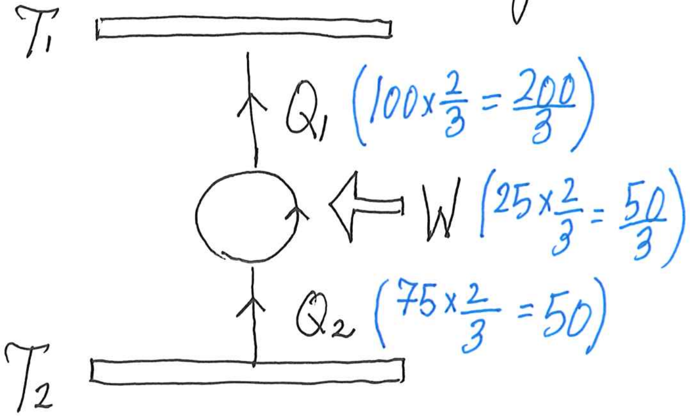
e.g. $\eta = 1 - \frac{Q_2}{Q_1} = 0.25$

Someone's claim of a More Efficient Engine



$\eta' = 1 - \frac{Q_2'}{Q_1'} = 0.5$ (better one!)

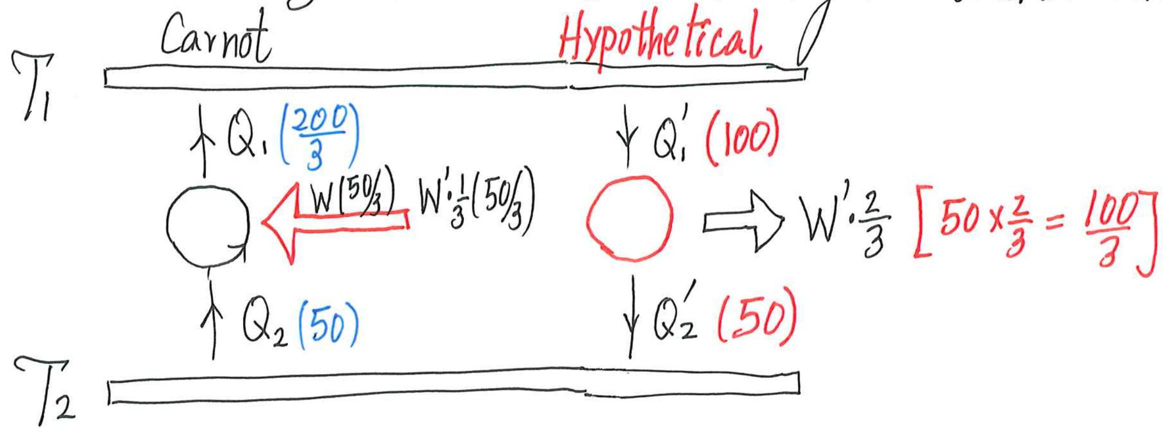
(i) Scale down Carnot engine to $\frac{2}{3}$ (size) and run it backwards as refrigerator



$W' = 50$

$\underbrace{W' \times \frac{1}{3} \left(\frac{50}{3}\right)}_{\text{part of } W' \text{ to drive Carnot engine backwards}}$ $\quad \underbrace{W' \times \frac{2}{3} \left(\frac{100}{3}\right)}_{\text{remaining part}}$

(ii) Use $W' \times \frac{1}{3}$ to run Carnot engine backwards



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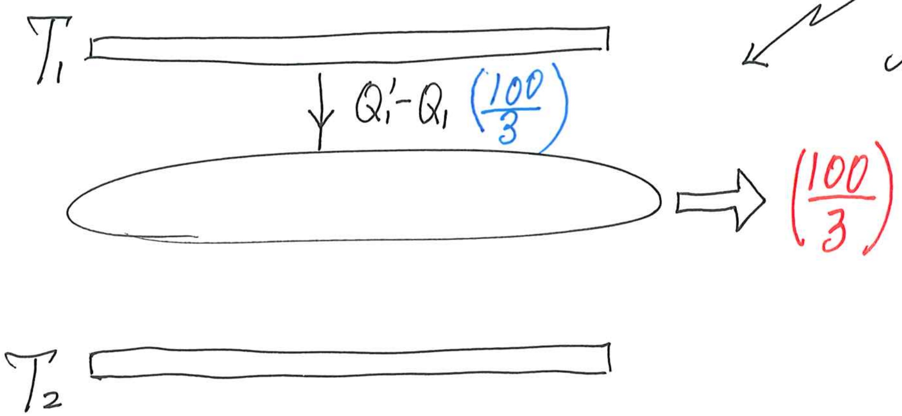

An engine whose sole effect is to extract heat from a single body at T_1 and the performance of equivalent amount of work

$\therefore$ The suggestion of an engine more efficient than the Carnot engine also violates the Kelvin-Planck statement of 2nd Law.

Discussions on 2nd Law end here