

Thermodynamics

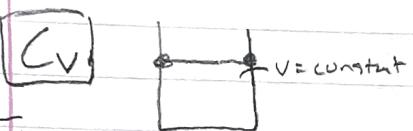
C_V and C_P

Specify heat capacity



C_P exerts a constant force over a constant area so the pressure on the system is constant

$$C_P = \lim_{Q \rightarrow 0} \frac{Q}{\Delta T} \Big|_{P=\text{constant}}$$



$$C_V = \lim_{Q \rightarrow 0} \frac{Q}{\Delta T} \Big|_{V=\text{constant}}$$

from $Q = C \Delta T$
amount of heat flow is the change in T + a value that depends on object

First law of thermodynamics

$$\downarrow W = \int F dx = \int P A dx = \int_{V_i}^{V_f} P dV$$

$$\text{internal energy} = \Delta U = Q - W$$

↳ tells you heat is transferred to the system by work

$$C_P = \lim_{Q \rightarrow 0} \frac{Q}{\Delta T} \Big|_{P=\text{constant}}$$

$$\text{and } Q = \Delta U + W = U_f - U_i + P \int_{V_i}^{V_f} dV = U_f - U_i + P(V_f - V_i)$$

$$= \lim_{\Delta T \rightarrow 0} \frac{H(T+\Delta T, P) - H(T, P)}{\Delta T}$$

$$Q = (U_f + PV_f) - (U_i + PV_i) = H_f - H_i = \Delta H$$

$$= \frac{\partial H(T, P)}{\partial T} \rightarrow C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

$$C_V = \lim_{Q \rightarrow 0} \frac{Q}{\Delta T} \Big|_{V=\text{constant}} \rightarrow W = \int_{V_i}^{V_f} P(V) dV = 0 \text{ no work done}$$

$$Q = \Delta U = U(T_f, V) - U(T, V) = U(T+\Delta T, V) - U(T, V)$$

$$C_V = \lim_{Q \rightarrow 0} \frac{Q}{\Delta T} \Big|_{V=\text{constant}} = \lim_{\Delta T \rightarrow 0} \frac{U(T+\Delta T) - U(T)}{\Delta T} \Big|_{V=\text{constant}} = \left(\frac{\partial U}{\partial T} \right)_V = C_V$$

$$\{ C_P - C_V = ? \} \text{ using } PV = nRT \Rightarrow V(T, P) = \frac{nRT}{P} \text{ and } H(T, P) = U(T) + PV(T, P)$$

* Note U is normally a func of temperature and pressure but for ideal gas its just $U(T)$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{dU(T)}{dT} + nR \quad \text{and} \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$$

$$C_P - C_V = \frac{dU(T)}{dT} + nR - \frac{dU(T)}{dT} = nR$$

If $U(T, V)$ then it's more complicated

$$U_{\text{univari}} = M C_v T$$

$$\hookrightarrow U(T, V) = U_{\text{univari}}(V) + U_{\text{univari}}(T) \quad \text{and} \quad U_{\text{univari}} = \phi_0 + b_0 \left[\ln \left(\frac{V}{V_0} \right) - 1 \right] V$$

$$\hookrightarrow U(T, V) = \phi_0 + b_0 \left[\ln \left(\frac{V}{V_0} \right) - 1 \right] V + M C_v T$$

then:

$P = -b_0 \ln \left(\frac{V}{V_0} \right) + \alpha_0 T$
$V = V_0 e^{\frac{(\alpha_0 T - P)}{b_0}}$

the goal is to calculate $(C_p - C_v)$

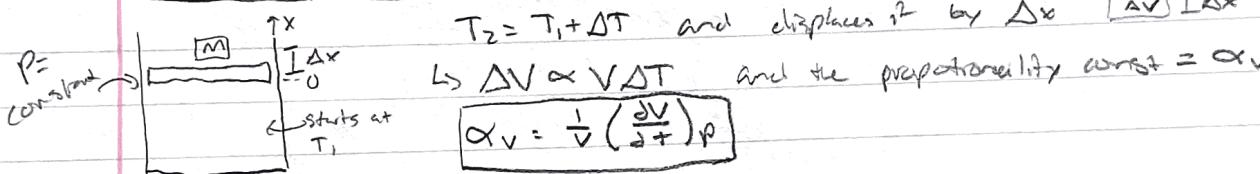
$$H(T, P) = U(T, V) + PV(T, V) \leftarrow \text{for } C_p \text{ plug everything in and take parts}$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P = \frac{\alpha_0}{b_0} TV + M C_v$$

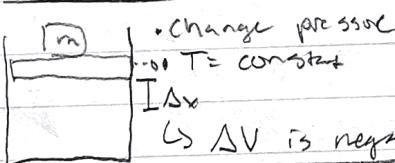
$$C_v = \left(\frac{\partial U}{\partial T} \right)_{V=\text{const}} = M C_v$$

$$\boxed{C_p - C_v = \frac{\alpha_0}{b_0} TV}$$

Thermal expansion coeff



Bulk modulus



$\hookrightarrow -V \Delta P \propto \Delta V \rightarrow$

$$B_T = -V \left(\frac{\partial P}{\partial V} \right)_T$$

* good for iron but terrible approx for air

plugging into $C_p - C_v = \frac{\alpha_0^2}{b_0} TV = \alpha_v^2 B_T TV$

Not be clear; apply some math tricks

independent of sample size

heat capacity at constant volume $C_v \rightarrow \text{specific heat } C_v = \frac{C_v}{m}$

$$\frac{C_v}{m} = C_v^m$$

heat capacity at constant pressure C_p sum rule applies?

$$Q = M C_v^m \Delta T$$

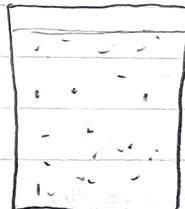
depends on material

Internal Energy and the first law of thermodynamics

ΔU describes the state of the system, its units are energy.

↳ First law says: $\Delta U = Q - W$ (conservation of energy) $Q = \text{heat}$, $W = \text{work}$

- Work is the energy transferred to the system. (compressing a piston etc.)
- Heat is the energy of the particles bouncing around



Internal energy is literally all the energy in a system
KE of all the atoms/molecules, Potential energy too
for ideal gases ≈ 0

$$U(T, V) \rightarrow U(T)$$

Let's say internal energy is changing; ΔU , then energy is being transferred to it or away from it (by work) then you get

$$\Delta U = Q - W, \text{ makes sense if } W=0 \text{ then } Q=\Delta U$$

(V is volume)
and $W = \int_{V_i}^{V_f} P(V) dV$,

if Volume decreases then $\Delta U = Q - (-W)$ (does work for you)
WORK BEING DONE BY SYSTEM

and $Q = n c_v \Delta T = m c_v \Delta T$

also $C_p - C_v = R$ (non-specific heat) $C_p - C_v = nR$
(* Dont forget $PV = nRT$ when relates P, V, T)

Constant volume \rightarrow isochoric process: $W = \int_{V_i}^{V_f} P dV = 0$ thus $\Delta U = Q$

Constant pressure \rightarrow isobaric process: $W = P \int_{V_i}^{V_f} dV = P \Delta V$ so $\Delta U = Q - P \Delta V$

Constant temperature \rightarrow Isothermal process: $W = \int_{V_i}^{V_f} P(V) dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$

↳ ALSO! for ideal gases $\Delta U(T) = 0$, the temperature is constant so the KE of all the molecules stays constant, thus:

$$Q = W = nRT \ln\left(\frac{V_f}{V_i}\right)$$

which is the total energy of the system for ideal gases

Quick notes:

The total heat of a system is just summing the energies, what I mean is for systems where ΔS is just two bodies combining then:

Usually we consider
it's to find
temp change
if some
Q

$$Q_1 + Q_2 + Q_3 + Q_n = 0 \quad \text{where } Q = mc\delta T$$

or another of form

Back to first law! there's another process where there is no heat exchanged in or out of the system, called adiabatic process

$$\Delta U = Q^0 - W \quad * \text{the transfer in energy is by work not heat}$$

↳ useful for engines where you only want the system to transfer energy by work

Taylor expand $\Delta U = \frac{U(T, V)}{C_V} \Delta T + \frac{\left(\frac{\partial U}{\partial V}\right)_T \Delta V}{0 \text{ for an ideal gas}}$ first order Taylor expansion

So $\Delta U = nC_V \Delta T$ and $W = \int_{V_0}^{V_0 + \Delta V} P(V) dV = P \Delta V$ for small changes in volume $P \approx \text{const}$

$$\hookrightarrow nC_V \Delta T + P \Delta V = 0 \quad \rightarrow \quad nC_V \frac{\Delta T}{T} + nR \frac{\Delta V}{V} = 0 \quad \rightarrow \quad \frac{1}{V} \frac{dV}{dt} = -\frac{C_V}{R} \frac{1}{T}$$

Solve. $\ln V = -\frac{C_V}{R} \ln T + \text{const}$, $\frac{C_P}{C_V} = \frac{C_P}{C_V} = \gamma = \text{adibatic constant}$

$$\hookrightarrow \frac{C_P - C_V}{C_V} = \frac{R}{C_V} \rightarrow \gamma - 1 = \frac{R}{C_V}$$

$\hookrightarrow (\gamma - 1) \ln V + \ln(T) = \text{const}$

$$\boxed{V^{\gamma-1} T = \text{constant}} \\ PV^\gamma = \text{constant}$$

↳ useful to do stuff like calculate work

$$PV^\gamma = \text{constant} = P_0 V_0^\gamma \rightarrow W = \int_{V_0}^{V_f} P(V) dV$$

$$P = P_0 \frac{V_0^\gamma}{V^\gamma}$$

Irreversible and Reversible Process

(ex) w/ electrical systems,

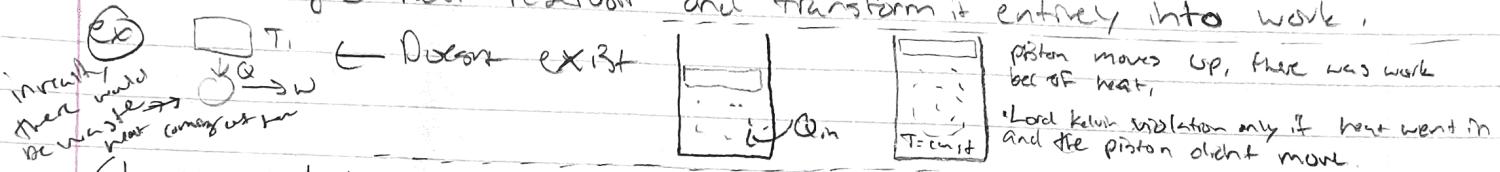


$$V_E = RI \rightarrow W = -RI^2 \Delta t$$

by $\Delta U = Q - W$, nothing coming into system, $\Delta U = 0$ so $Q = W = -RI^2 \Delta t$

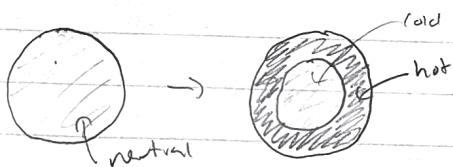
2nd LAW OF THERMODYNAMICS

Kelvin: There is no process whose only effect is to accept heat from a single heat reservoir and transform it entirely into work.



Claussus: We don't see a spontaneous transfer of heat from a colder system to a hotter one.

↪ we don't see ice form in the middle of water.



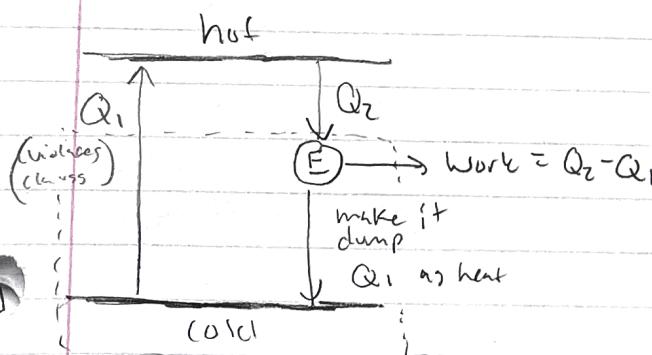
don't see heat from a colder system go to hotter one

→ we do observe heat flow to cold. If there is ice in cup, heat from water goes into ice, we see hot → cold

These are esp
state
ments

Proof:

1 violate Claussus

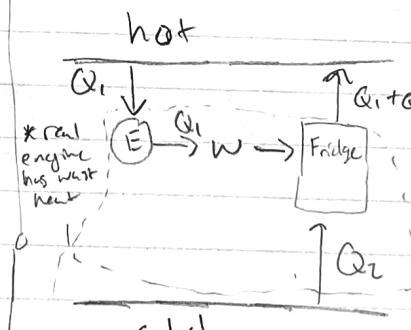


↑ box produces work

w/out any wasted heat

& violates Lord Kelvin

2 violate Kelvin



Q_1 goes in

and $Q_2 + Q_1$

comes out of cold, violates

Claussus, heat from a cold body going to a hot one

thus by violating Kelvin we violate Claussus and by violating Claussus we violate Kelvin

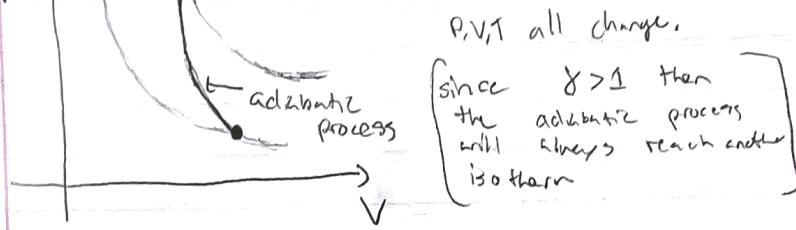
Thermo
Part 2

Adiabatic process is a pressure, volume, temperature relation that relies on the fact there is no heat transfer in or out of the system.

Specifically, $V^{\gamma-1}T = \text{const.}$ and $PV^\gamma = \text{const}$ where $\gamma = \frac{C_p}{C_v}$

On a curve

where the contour lines represent Isotherms.



$$\begin{aligned} h + \text{pressure in air} &\rightarrow [P(h) - P_{\text{atmos}}] = \frac{Mg}{A} \\ \text{mass within } \Delta h & \\ P(h) &= P(h + \Delta h) + \frac{Mg}{A}, \quad M = \text{gas} \text{Var} = \rho \text{Var} \Delta A \\ P(h) - P(h + \Delta h) &= P(h + \Delta h) + \frac{\rho \text{Var} \Delta h g}{A} = P(h + \Delta h) + \rho \Delta h g \end{aligned}$$

• find $\rho \rightarrow PV = nRT \rightarrow \frac{PV}{M} = \frac{n}{m} RT \Rightarrow \rho = \frac{M}{n} \frac{P}{RT}$

$$-\frac{P(h) + P(h + \Delta h)}{\Delta h} = -\frac{M}{n} \frac{P}{RT} g \rightarrow \frac{dP}{dh} = -\frac{M}{n} \frac{g}{R} \frac{P}{T}$$

- * the goal of this is to figure out how T changes with h , $\frac{dT}{dh}$
- air transport is adiabatic so we can use the pressure, volume, Temp relations

$$\hookrightarrow V = \frac{nRT}{P} \text{ and } PV^\gamma = \text{const} \rightarrow \frac{T^\gamma}{P^{\gamma-1}} = \text{const} \text{ now do } \frac{d}{dh} \left(\frac{T^\gamma}{P^{\gamma-1}} \right) = 0$$

$$\gamma \frac{T^\gamma}{P^{\gamma-1}} \cdot \frac{1}{T} \frac{dT}{dh} - (\gamma-1) \frac{T^\gamma}{P^{\gamma-1}} \frac{1}{P} \frac{dP}{dh} = 0 \rightarrow \frac{dT}{dh} = (\gamma-1) \frac{1}{P} \frac{dP}{dh} \quad \begin{array}{l} \text{plug in from} \\ \text{air density} \end{array}$$

constant (so divide out) constant

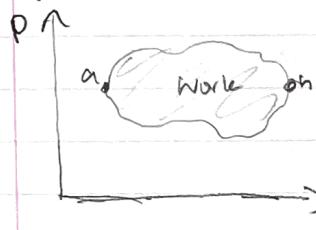
$$\frac{dT}{dh} = -\frac{(\gamma-1)}{\gamma} \frac{M g}{n R} \quad \leftarrow \begin{array}{l} \text{tells you how} \\ \text{temperature changes} \\ \text{with height in air} \end{array}$$

Cyclic Process

- periodically returns to initial state so

$$\Delta U = 0 \text{ then } Q = W$$

graphically

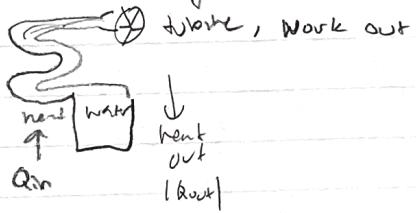


forms a closed loop in PV space

$$W = \int P dV$$

area

Engine B cycle: absorbs heat $|Q_{in}|$ and gets rid of $|Q_{out}|$ and does a positive amount of work

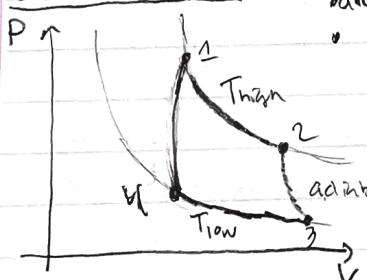


Energy efficiency

$$\eta = \frac{\text{work out}}{\text{heat in}} = \frac{W}{|Q_{in}|} = \frac{|Q_{in}| - |Q_{out}|}{|Q_{in}|}$$

Carnot cycle (constant gas)

along the lines the temperature is constant, so thermal

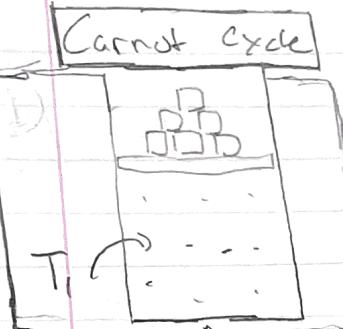


- $1 \rightarrow 2$ goes from lower volume to higher volume
 - ↳ expansion, so P goes down, all at constant T
 - ↳ heat flows into the system to keep it Isothermal, $T_h = T_1 = T_2$

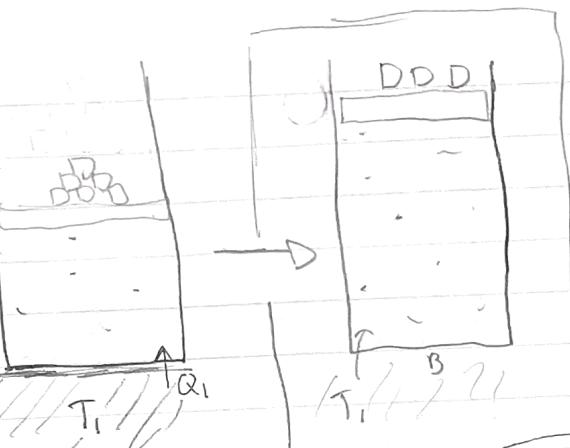
- $2 \rightarrow 3$ adiabatic expansion process, no heat leaves the system, but T ~~constant~~ decreases
- $3 \rightarrow 4$ is compression $T_{low} = T_3 = T_4$
- $4 \rightarrow 1$ adiabatic compression process, no heat leaves the system but T increases

Brief overview more in depth
On other page

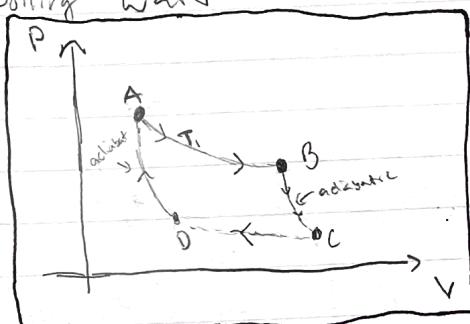
* take mass off
 * keep at constant temperature
 * heat goes in



reservoir of T_1 , keep temperature constant and thus ΔU_1 . think of like trying to change temp of ocean w/ one cup of boiling water



for part B



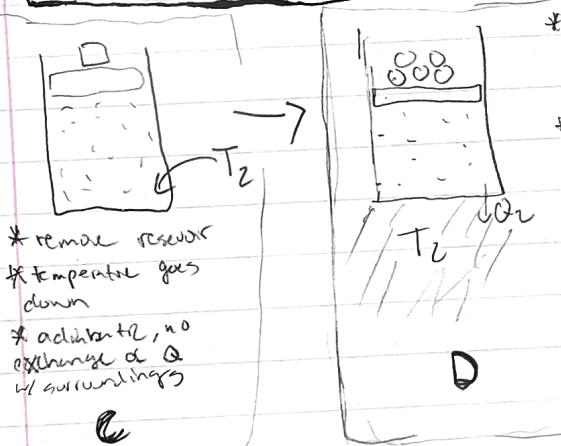
* move along an isotherm
 * work done by system B area under curve $\int P dV$
 $\Delta U = Q_1 - W_{AB} \rightarrow Q_1 = W_{AB}$

PBtan goes up

V increases P decreases

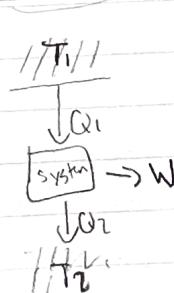
vT goes down

I take much off



* temperature of system will want to go up but T_2 keeps it at constant temperature
 * work done to the system

$Q_2 = W_{CD}$ since ΔV is neg $Q_2 = \text{negative}$



$$Q_1 - Q_2 = W_{AB+CD}$$

makes sense because $Q_1 \rightarrow Q_{in}$ and $Q_2 \rightarrow Q_{out}$
 if it returns back to its original ΔU then work done by the system is $Q_1 - Q_2$



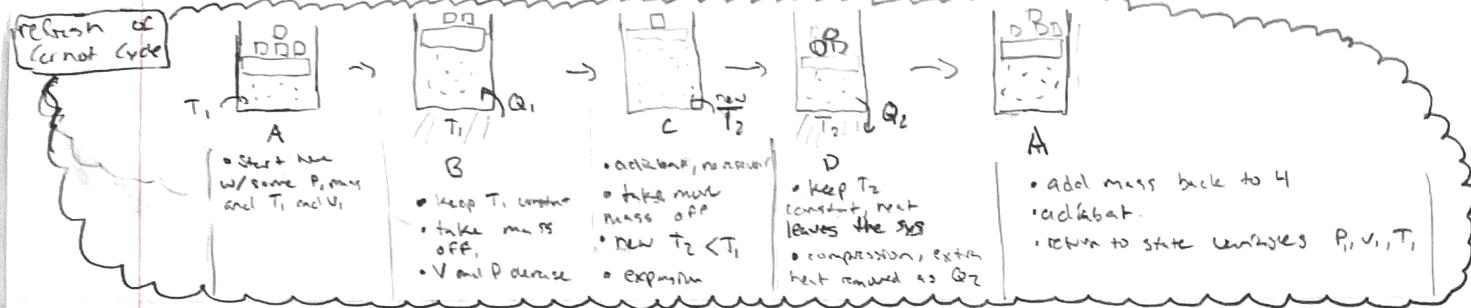
more precisely: $|Q_1| = |Q_{in}| = |W_{AB}|$

$$|Q_2| = |Q_{out}| = -|W_{CD}|$$

rewriting so we can look at total work \rightarrow

$$|Q_1| - |Q_2| = |W_{AB}| + |W_{CD}| = W_{tot}$$

heat left the system and work was done on the system



Efficiency

$$\eta = \frac{\text{Work out}}{\text{heat in}} = \frac{W}{Q_{in}}$$

$$\text{For Carnot: } W = |Q_{in}| - |Q_{out}| \rightarrow \eta = \frac{|Q_{in}| - |Q_{out}|}{|Q_{in}|}$$

* efficiency cares when heat is moved so not during adiabatic processes

↳ A → B and C → D is what we care about

$$A \rightarrow B: |Q_{in}| = W_{A \rightarrow B} = \int_{V_A}^{V_B} P dV = nRT_1 \int_{V_A}^{V_B} \frac{1}{V} dV = nRT_1 \ln\left(\frac{V_B}{V_A}\right) \quad (\text{work along an isotherm})$$

$$C \rightarrow D: |Q_{out}| = -Q_{D \rightarrow A} = -nRT_2 \ln\left(\frac{V_D}{V_C}\right) \quad \Rightarrow \quad - \int_{V_C}^{V_D} P dV$$

$$\eta = 1 - \frac{-nRT_2 \ln\left(\frac{V_D}{V_C}\right)}{nRT_1 \ln\left(\frac{V_B}{V_A}\right)}$$

but we can relate the volumes,

↳ relate from our other info, the adiabats. $V_B^{\gamma-1} T_1 = V_C^{\gamma-1} T_2$ and $V_B^{\gamma-1} T_2 = V_A^{\gamma-1} T_1$

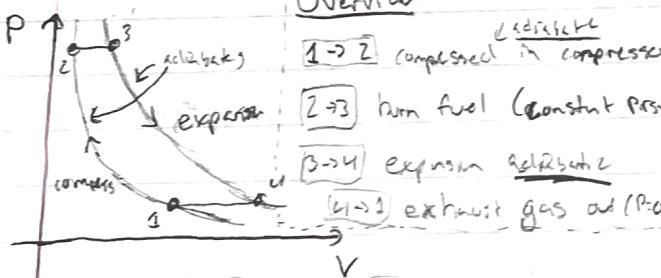
$$\therefore \frac{V_B^{\gamma-1}}{V_A^{\gamma-1}} = \frac{V_C^{\gamma-1}}{V_B^{\gamma-1}} \quad \text{Now} \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

use this in efficiency

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

Brunton-Joule Cycle (Gas turbine)

Overview



$$\eta = 1 - \frac{|Q_{out}|}{|Q_{in}|}$$

look at constant pressure processes 2 → 3 and 4 → 1

$$|Q_{in}| = Q_{2 \rightarrow 3} = nC_p(T_3 - T_2)$$

to not get Q 's
 ΔT sign wrong just
think of it as $T_{high} - T_{low}$
which is what affects the
efficiency the most

Plug in: $\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2}$, let's look at pressures because that's where compressor comes in

$$PV^{\gamma} = \text{const} \rightarrow \frac{T_2}{P_2^{\gamma-1}} = \text{const} \rightarrow \frac{T_2}{P_{2,3}^{\gamma-1/\gamma}} = \frac{T_1}{P_{1,4}^{\gamma-1/\gamma}} \quad \text{and} \quad \frac{T_3}{P_{2,3}^{\gamma-1/\gamma}} = \frac{T_4}{P_{1,4}^{\gamma-1/\gamma}}$$

Using these

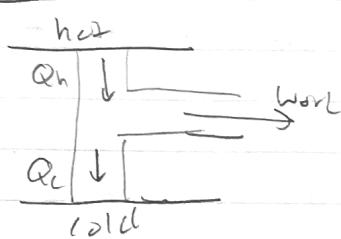
$$\boxed{\eta = 1 - \left(\frac{P_{1,4}^{\gamma-1/\gamma}}{P_{2,3}^{\gamma-1/\gamma}} \right)}$$

Carnot Cycle Theorem

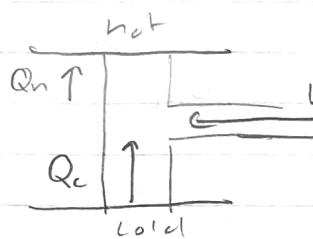
going to show:

- ① Energy efficiency of the Carnot Cycle is independent of working substance
- ② Any cyclic process that absorbs heat at one temperature and rejects heat at another temperature, and is reversible, has the energy efficiency of a Carnot Cycle.

Recall:



reversible



not

$$|Q_h| = |Q_c| + W_1$$

loses some energy
to get Q_h

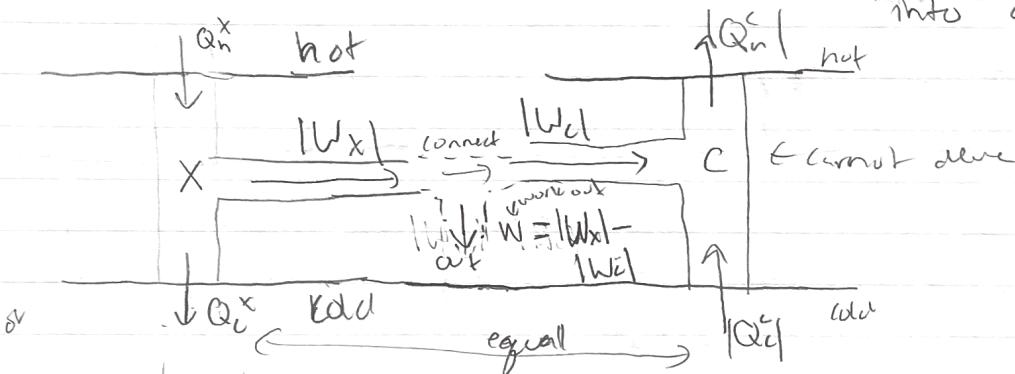
work

$$\text{Coef of performance} \quad \eta_p = \frac{|Q_h|}{|W_1|}$$

T_{hotest}

Let's say we have a $n_x > n_c$:

* Feed this n_x heat engine
into a heat pump.

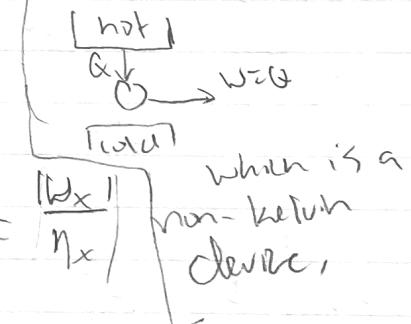


Make $|Q_h^x| = |Q_h^c|$ can always design thus

$$|W_x| = |Q_h^x| - |Q_c^x| \quad , \quad n_x = \frac{|W_x|}{|Q_h^x|} \rightarrow |Q_h^x| = \frac{|W_x|}{n_x}$$

$$|W_x| = \frac{|W_x|}{n_x} - |Q_c^x| \rightarrow |W_x| = \frac{n_x}{1-n_x} |Q_c^x|$$

* since $Q_h^x = Q_h^c$
* you are getting work
out of just the hot
thing



for a Carnot machine $|W_c| = \frac{n_c}{1-n_c} |Q_c^c|$ w/ $n_x > n_c$ then $|W_x| > |W_c|$

$W_{out} = |W_x| - |W_c| > 0$, getting work out of just getting a Q
from a heat reservoir, violates 1st law

$$3M - (M) = \text{# deer}$$

$$\dot{x}_i = (f^+ + M\eta)$$

$$\dot{x} = M\eta$$

Thus $\eta_x > \eta_c$ False

If you let X be the heat pump and the Carnot cycle operate like engine you get

$$\eta_c > \eta_x \text{ (obviously) False}$$

$$\text{thus } \eta_c = \eta_x$$

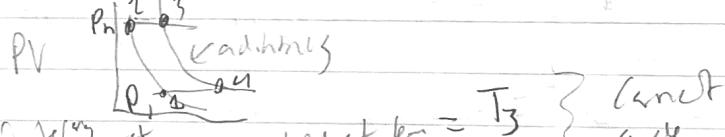
① Energy efficiency of Carnot Cycle is independent of the working substance

② Any cyclic process that absorbs heat at one temperature and rejects heat at another temperature, and is reversible has energy efficiency of Carnot cycle

If engine isn't reversible, like an engine it will always be less than η_c

= calculated other efficiencies because gas turbine, Otto cycle very 2 temp. levels, accept and reject heat at a range of temperatures

Consider gas turbine!



$$\eta = 1 - \left(\frac{P_1}{P_2} \right)^{\frac{r-1}{r}}$$

\rightarrow 0% entropy
the 100% cycle
to lowest
temp down

highest temp = T_3 } Carnot cycle
lowest temp = T_1 } heat rejection

$$\eta = 1 - \frac{T_1}{T_2}$$

$$\text{gas law} \quad T_3 = \Delta T + T_2$$

$$\eta_c = 1 - \frac{T_1}{T_3}$$

$$\eta_c = 1 - \frac{T_1}{\Delta T + T_2}$$

always better than Brayton

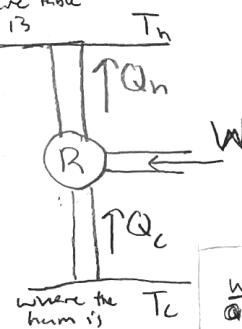
limit when $\Delta T \rightarrow 0$ but no heat loss
 $\Delta T \rightarrow 0$ but no heat loss
tot, no work

Heat Engines and Heat pumps w/ efficiencies and coefficients of performances respectively

Engine

$$n_E = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

— — — — —
where table
13



* Can't have alone, violates classical statement
of 3rd Law, need to put
in work to make this
happen.

$$(\text{coeff of performance}) = COP = \frac{\text{What we want}}{\text{What we pay}} = \frac{Q_c}{W}$$

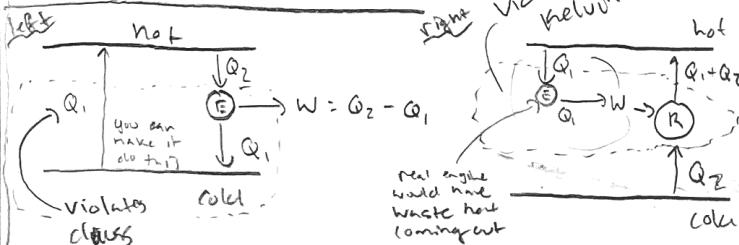
$$+ Q_n = Q_c + w \rightarrow \text{cp} = \frac{Q_n - w}{w} \frac{(1/\omega_n)}{(1/\omega_n)} = \frac{1 - \frac{w}{Q_n}}{\frac{w}{Q_n}}$$

$$LDP = \frac{1-\eta}{\eta}$$

* Lord Kelvin - There is no process whose only effect is to accept heat from a single reservoir and transform it entirely into work.

* Claussus - We don't ever see a spontaneous transfer of heat from a colder system to a hotter one.

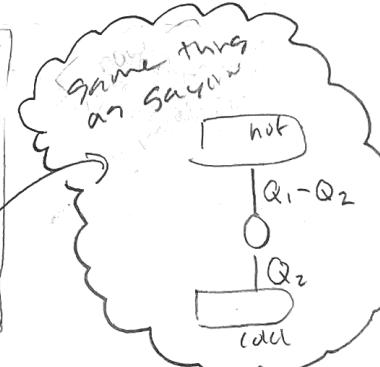
Examples of violations



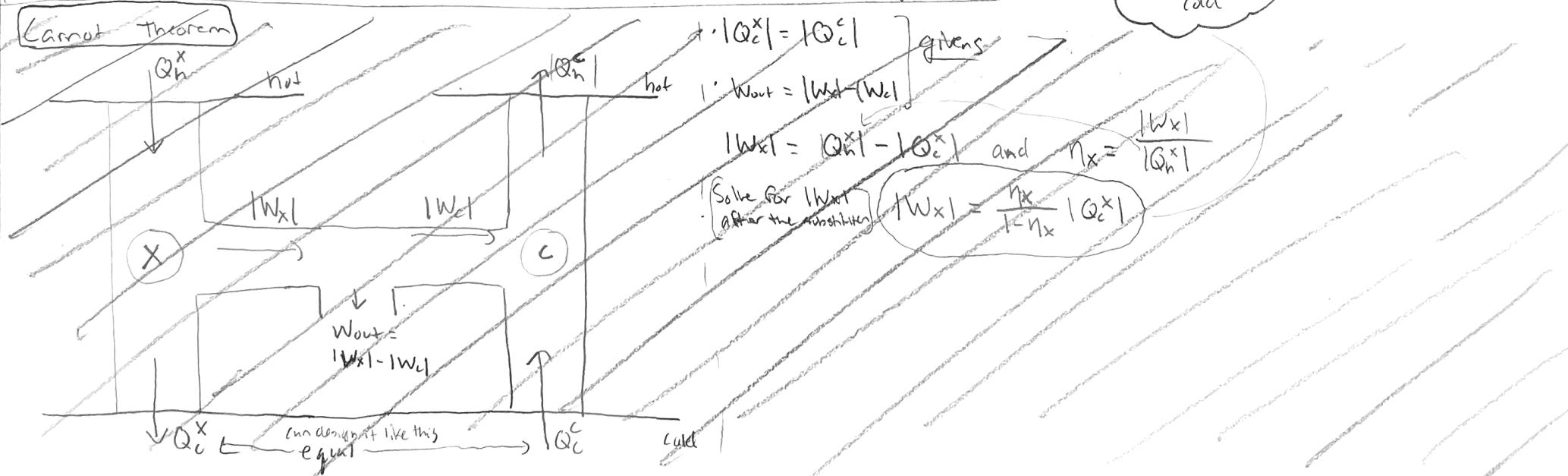
* also shows how they are equivalent statements?

↳ left produces work w/out any wasted heat
↳ also violates 1st law

↳ right Q_1 goes in and $Q_2 + Q_1$ comes out
 of cold, violates causality. Just look at
 ↳ Q_2 comes out of hot
 and $Q_2 + Q_1$ gets back in, so there
 is a spontaneous flow of heat Q_2 going into hot



Carnot Theorem

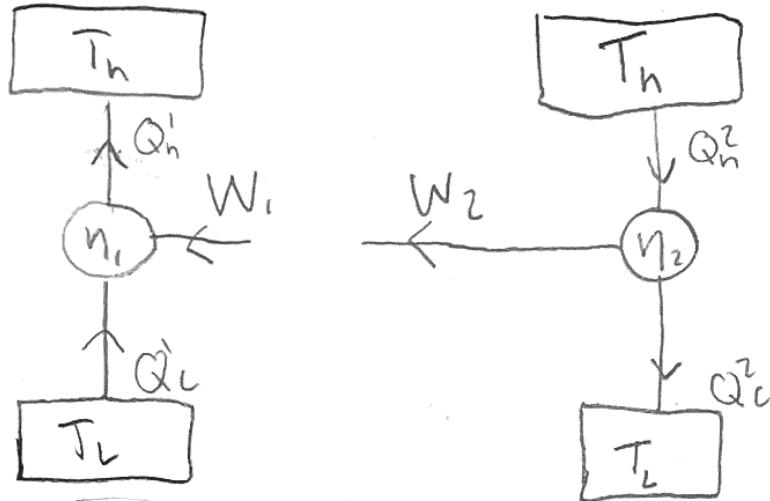


Carnot Theorem

- all reversible engines operating between the same two baths have the same η

$$\eta = 1 - \frac{T_c}{T_h} = 1 - \frac{Q_c}{Q_h}$$

[Proof by contradiction, assume you have two Carnot engines w/ different η]



Let's say $\eta_1 < \eta_2$:

and have the special case $W_1 = W_2$, the Carnot efficiency $\eta = W/Q_h$, $W/\eta_1 > W/\eta_2$

Step 1 $\eta_1 < \eta_2 \Rightarrow \frac{W}{Q_h^1} < \frac{W}{Q_h^2}$

thus $Q_h^1 > Q_h^2$ ①

Step 2 $\eta_1 = 1 - \frac{Q_c^1}{Q_h^1}$, $\eta_2 = 1 - \frac{Q_c^2}{Q_h^2}$

$\eta_1 < \eta_2$

$$1 - \frac{Q_c^1}{Q_h^1} < 1 - \frac{Q_c^2}{Q_h^2}$$

$$\frac{Q_c^1}{Q_h^1} > \frac{Q_c^2}{Q_h^2}$$

$$\frac{Q_c^1}{Q_h^1} > \frac{Q_c^2}{Q_h^2}$$

$$Q_c^1 > Q_c^2 \frac{Q_h^1}{Q_h^2}$$

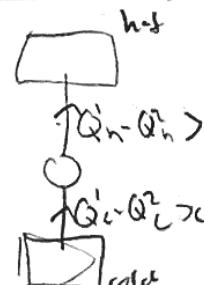
bigger than 1

so $Q_c^1 > Q_c^2$ was to be met

Taking note

① $Q_h^1 - Q_h^2 > 0$

② $Q_c^1 - Q_c^2 > 0$



Total work is 0

if $Q_h^1 - Q_h^2 > 0$ and

$Q_c^1 - Q_c^2 > 0$ then net heat flow from cold bath to hot bath. Violates Clausius