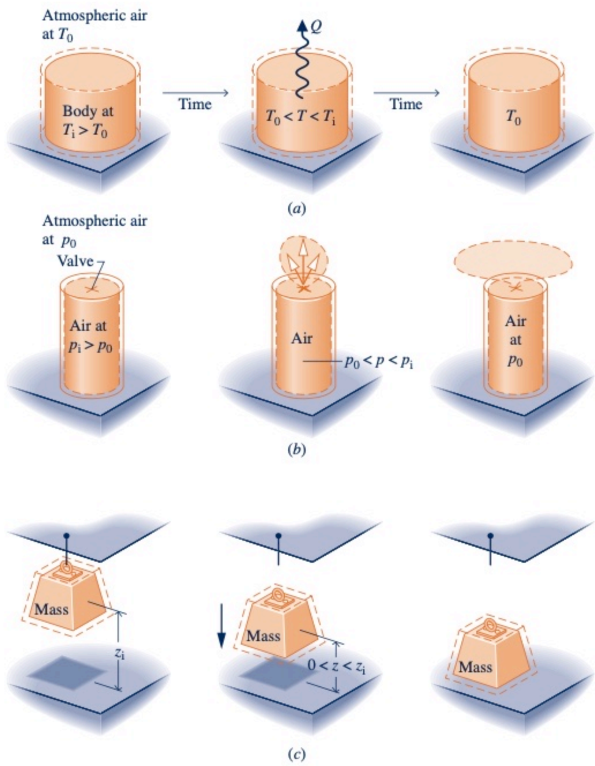
Thermo Ch. 5 Notes

Motivating the Second Law of Thermodynamics

- there is a definite direction for spontaneous processes
- below are illustrations of spontaneous processes and the eventual attainment of equilibrium w/ the surroundings



(a) SPONTANEOUS HEAT TRANSFER

an object an elevated temperature T_i placed in contact w/ atm air at temp T_0 eventually cools to temp of much larger surroundings

- $\downarrow U_{system}$ means $\uparrow U_{surr}$ and the inverse process would not take place spontaneously even though energy could be conserved: the U_{surr} would not $\downarrow$ spontaneously while the body warmed from T_0 to initial temp

(b) SPONTANEOUS EXPANSION

air held at high pressure P_i in closed tank flows spontaneously to lower-pressure surroundings at P_0 when the interconnecting valve is opened

- eventually, fluid motions cease and all of air is @ same press as surr
  - ↳ inverse process would not take place spontaneously even though energy could be conserved: air would not flow spontaneously from surroundings at P_0 into tank, returning press to initial

(c) FALLING MASS

A mass suspended by a cable at elevation z_i falls when released; when it comes to rest, PE of mass in its initial condition appears as an increase in the U_{mass} and U_{surr} (cons of energy)

→ eventually mass also comes to temp of its much larger surroundings

→ the inverse process would not take place spontaneously, even though energy could be conserved: mass would not return spontaneously to its initial elevation while its U and/or that of surroundings decreases

* In each case considered, the initial condition of the system can be restored but not in a spontaneous process

* when left alone systems tend to undergo spontaneous changes until a condition of equilibrium is achieved, both internally and with their surroundings

↳ whether the process is rapid or slow, must satisfy cons of energy but this alone is insufficient to determine final state [need the 2nd Law!]

Aspects of the 2^{nd} Law

1. predict direction of processes
2. establishing conditions for equilibrium
3. determining the best theoretical performance of cycles, engines, and other devices
4. evaluating quantitatively the factors that preclude the attainment of the best theoretical performance level
5. defining a temperature scale independent of the properties of any thermometric substance
6. developing means for evaluating properties such as u and h in terms of properties that are more readily obtained experimentally

→ no single statement of the 2^{nd} Law brings out each of its many aspects

Statements of the Second Law — 3 alternative statements

(1) Clausius } traditional
(2) Kelvin-Planck (KP) } traditional
(3) entropy

Clausius Statement — it is impossible for any system to operate in such a way that the sole result would be an energy xfer by heat from a cooler to a hotter body

→ does not rule out possibility of xfering energy by heat from a cooler body to a hotter body bc this is exactly what refrigerators and heat pumps accomplish

→ "sole result" suggests when a heat xfer from a cooler body to a hotter body occurs, there must be other effects w/in the system accomplishing the heat xfer, its surroundings, or both

→ if system operates in a thermodynamic cycle, its initial state is restored after each cycle, so the only place that must be examined for such other effects is its surroundings

Thermal Reservoir — special kind of system that always remains at constant temperature even though energy is added or removed by heat xfer

→ an idealization but can be approximated (by Earth's atm, large bodies of H_2O, etc)

→ extensive properties of a thermal reservoir such as internal energy can change in interactions w/other systems even though the reservoir temp remains constant

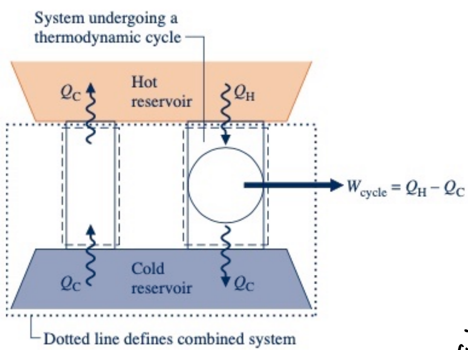
Kelvin-Planck Statement — it is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat xfer from a single thermal reservoir

→ does not rule out possibility of a system developing a net amount of work from a heat xfer drawn from a single reservoir (it only denies this possibility if the system undergoes a thermodynamic cycle

$W_{cycle} = Q_{cycle}$ → a system undergoing cycle while communicating thermally w/ single reservoir can't deliver a net amount of work to its surroundings: the net work of the cycle cannot be positive

→ however, K-P doesn't rule out possibility that there's a net work xfer of energy to the system during cycle or that net work is zero

∴ K-P says $W_{cycle} \leq 0$ (single reservoir)



• system on left xfers energy Q_C from cold to hot w/out other effects VIOLATES CLAUSIUS

• system on right operates in a cycle while receiving Q_H ($> Q_C$) from hot, rejecting Q_C to cold, and delivering work W_{cycle} to surroundings

• combined system can be regarded as cycle, receives energy ($Q_H - Q_C$) by heat xfer from single reservoir (hot) and produces equivalent amount of work VIOLATES KP

thus, a violation of Clausius implies violation of KP, and violation of KP implies violation of Clausius

Entropy Statement of the 2nd Law

• entropy is extensive property

[change in the amount of entropy contained w/in the system during some time interval] = [net amount of entropy xferred in across the system boundary during the time interval] + [amount of entropy produced w/in the system during the time interval]

• unlike mass & energy, which are conserved, entropy is produced/generated w/in systems whenever nonidealities (called irreversibilities) such as friction are present

→ it is impossible for any system to operate in a way that entropy is destroyed entropy may be positive, or zero, but never ⊖

Irreversible and Reversible Processes

irreversible – a process is irreversible if the system and all parts of its surroundings cannot be exactly restored to their respective initial states after the process has occurred.

reversible – a process is reversible if both the system and surroundings can be returned to their initial states

The 2nd Law can be used to determine whether process is ir/reversible

Irreversible processes normally include one or more of the following irreversibilities

1. heat xfer through finite temp diff
2. unrestrained expansion of gas or liquid to lower pressure
3. spontaneous chemical rxn
4. spontaneous mixing of matter at diff compositions or states
5. friction
6. electric current through a resistance
7. magnetization or polarization w/hysteresis
8. inelastic deformation

↳ suggests that all processes are irreversible

→ there are internal/external irreversibilities

Reversible Processes

- a system and all parts of surroundings can be restored to their exact initial states after the process has taken place
- purely hypothetical
  - ↳ there can't be spontaneous heat xfer through a finite temp diff, an unrestrained expansion of gas or liquid, etc

Internally Reversible Processes

- process for which there are no irreversibilities w/in the system, but irreversibilities may be located in surroundings

→ we assume no internal irreversibilities present w/in a thermal reservoir

→ every process of a thermal reservoir is internally reversible

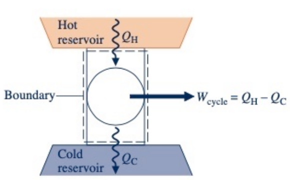
KP now takes the form:

$$W_{cycle} \leq 0 \begin{cases} < 0 : \text{internal irreversibilities present} \\ = 0 : \text{no internal irreversibilities} \end{cases} \quad \text{(single res.)}$$

Second Law Aspects of Power Cycles Interacting w/two Reservoirs

- system that executes cycle w/two th. reservoirs and dev. net work

$$\eta_{th} = \frac{W_{cycle}}{Q_H} = 1 - \frac{Q_C}{Q_H}$$



note: if $Q_C = 0$, $\eta_{th} = 100\%$ but this method of operation violates K-P and ∴ not allowed

η_{th} MUST BE < 100% FOR POWER CYCLES

↳ only portion of Q_H can be obtained as work, and remainder, Q_C, must be discharged as heat xfer to cold res.

The Carnot Corollaries

1. thermal efficiency of an irreversible power cycle is always < thermal eff. of rev. power cycle when each operates between same two thermal reservoirs.
2. all reversible power cycles operating between same two thermal reservoirs have the same thermal eff.

Second Law Aspects of Refrigeration & Heat Pump Cycles Interacting w/ two Reservoirs

refrigeration cycle C.O.P.

$$\beta = \frac{Q_c}{W_{cycle}} = \frac{Q_c}{Q_H - Q_c}$$

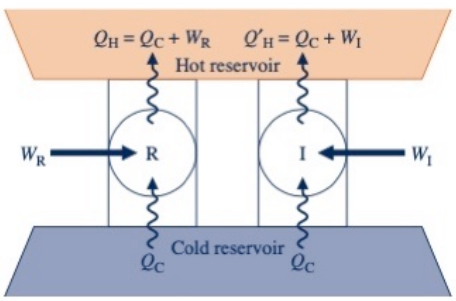
heat pump C.O.P.

$$\gamma = \frac{Q_H}{W_{cycle}} = \frac{Q_H}{Q_H - Q_c}$$

Corollaries of 2nd Law for Refrigeration + Heat Pump cycles

1. C.O.P of an irreversible refrigeration cycle is always < C.O.P of a reversible refrigeration cycle when each operates between same two thermal reservoirs
2. all reversible refrigeration cycles operating between same two thermal reservoirs have same C.O.P.

↳ these are the same for heat pump



R = reversible ref. cycle
I = irreversible ref. cycle

- R + I remove same energy Q_c
- I requires $W_I > W_R$ input and thus will have smaller β than R

- all rev. Ref cycles operating between same two reservoirs must ∴ then have same β

$$\left(\frac{Q_c}{Q_H}\right)_{rev\ cycle} = \frac{T_c}{T_H} \quad \text{(kelvin/Rankine)}$$

Maximum Performance Measures for Cycles Operating Between Two Reservoirs

Power cycles

- thermal eff of system undergoing rev. power cycle while operating between thermal res at temp T_H and T_c

$$\eta_{max} = 1 - \frac{T_c}{T_H} \Leftarrow \text{CARNOT EFFICIENCY}$$

→ this is the th. eff. of all rev. power cycles operating between T_c and T_H, and max. eff. of any power cycle can have while operating between the two reservoirs

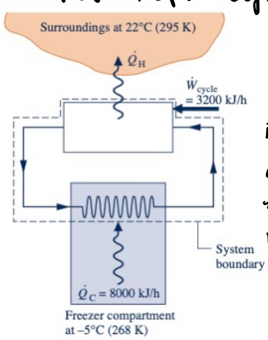
→ value of carnot efficiency ↑ as T_H ↑ and/or T_c ↓

Refrigeration + Heat Pump Cycles

- rev. ref. cycle/heat pump: Q_C represents heat added to cycle from cold res at temp T_C and Q_H is heat discharged to hot res. at temp T_H

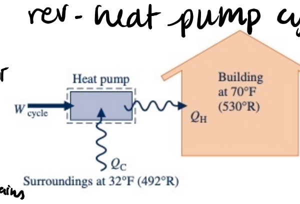
$$\beta_{max} = \frac{T_C}{T_H - T_C} \qquad \gamma_{max} = \frac{T_H}{T_H - T_C}$$

rev. ref. cycle



steadily circulating refrigerant at low temp through passages in the walls of freezer compartment, a fridge maintains freezer compartment at -5°C when air surrounding fridge is at 22°C

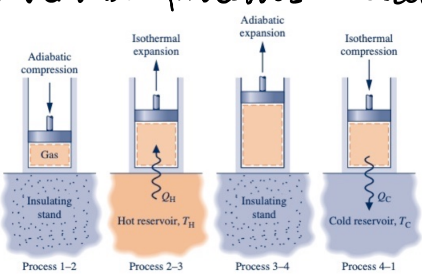
rev. heat pump cycle

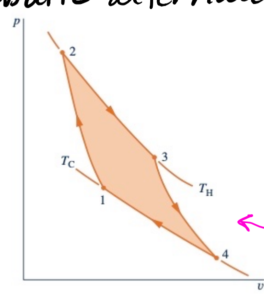


building requires $5(10^5)$ Btu/day to maintain its temp at 70°F when outside temp is 32°F

CARNOT CYCLE

system executing the cycle undergoes a series of four internally reversible processes: 2 adiabatic alternated w/ 2 isothermal processes





← carnot power cycle executed by a gas in a piston-cylinder assembly

← *enclosed area = net work developed by cycle per unit mass

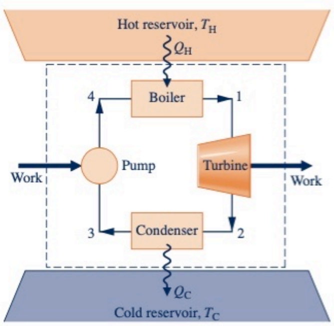
1→2: gas compressed adiabatically to state 2 where temp is T_H
- area under 1→2 represents work done per unit mass to compress the gas in this process

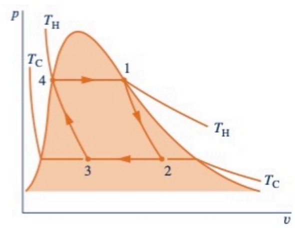
2→3: assembly placed in contact w/ res at T_H, gas expands isothermally while receiving energy Q_H from hot reservoir by heat xfer
- for heat xfer to be reversible, diff between gas temp and temp of hot reservoir must be very small, and since res. temp remains constant, implies that temp of gas also remains constant (same can be said for 4→1)
- area under 2→3 and 3→4 represent work done per unit mass by gas as expands in these processes

3→4: placed on insulating stand and gas allowed to continue to expand adiabatically until temp drops to T_C

4→1: in contact w/ cold res at T_C, gas compresses isothermally to its initial state while it discharges energy Q_C to cold res by heat xfer
- area under is work/mass to compress gas

CARNOT CYCLE OF SIMPLE VAPOR POWER PLANT





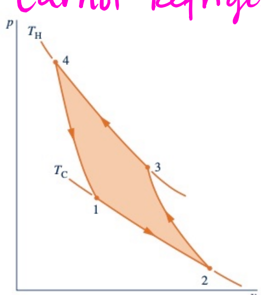
→ as H_2O flows through boiler, a <u>change of phase</u> from liquid to vapor at constant temp T_H occurs as a result of heat xfer from hot reservoir
- since temp ct, pressure also ct

→ steam exiting boiler expands adiabatically through turbine and work is developed
- temp ↓ to temp of cold res. T_c and there's accompanying ↓ pressure

→ as steam passes through the condenser, heat xfer to cold res occurs and some of vapor condenses at ct temp T_c
- since temp ct, pressure also ct as H_2O passes thru condenser

→ pump (or compressor) receives a 2-phase liquid-vapor mixture from condenser and returns it adiabatically to state @ the boiler entrance
- requires W input to ↑P, T↑ from T_c to T_H

Carnot Refrigeration and Heat Pump Cycles



Carnot refrigeration or heat pump cycle executed by gas in a piston-cylinder assembly

→ if carnot power cycle is operated in opp direction (as shown here), magnitudes of energy xfers remain same but opp. directions ... regarded as rev. ref/heat pump cycle

1→2: gas expands <u>isothermally</u> at T_c while <u>receiving</u> energy Q_c

2→3: gas compressed <u>adiabatically</u> until its temp is T_H

3→4: gas compressed <u>isothermally</u> at T_H while it <u>discharges</u> Q_H

4→1: gas expands <u>adiabatically</u> until temp ↓ to T_c

* ref/heat pump effect can be accomplished in a cycle only if a net work input is supplied to system executing cycle – shaded area represents net work input per unit mass

Carnot cycle summary

1. carnot cycle **always** has the same four internally reversible processes: 2 adiabatic alternated w/ 2 isothermal processes
2. thermal efficiency of Carnot power cycle is **always** given in terms of temp evaluated on kelvin/Rankine
3. C.O.P. of carnot ref. and heat pump cycles are **always** given in terms of temp evaluated on kelvin/Rankine

CLAUSIUS INEQUALITY

- applicable to **any** cycle w/out regard for the body, or bodies, from which the cycle receives energy by heat xfer or to which the cycle rejects energy by heat xfer

for any TD cycle:

$$\oint \left(\frac{\delta Q}{T}\right)_b \leq \phi$$

δQ = heat xfer at a part of system boundary during portion of cycle
T = abs. temp at that part of boundary
* like K-P...

→ equality when there are no internal irreversibilities as system executes the cycle
→ inequality applies when internal irreversibilities are present

$$\oint \left(\frac{\delta Q}{T}\right)_b = -\sigma_{cycle}$$

σ_{cycle} ⊕ when internal irreversibilities present
$\sigma_{cycle} = \phi$ when no internal irreversibilities present
σ_{cycle} can never be ⊖

$\sigma_{cycle} = \phi$ no irreversibilities present w/in system

$\sigma_{cycle} > \phi$ irreversibilities present w/in system

$\sigma_{cycle} < \phi$ impossible

σ_{cycle} can be interpreted as entropy produced (generated) by internal irreversibilities during the cycle