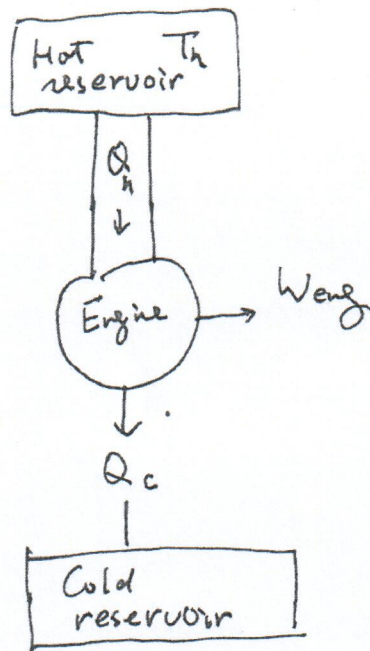Chap 22.   (Chapter 21 for 10ed. of Serway)

updated

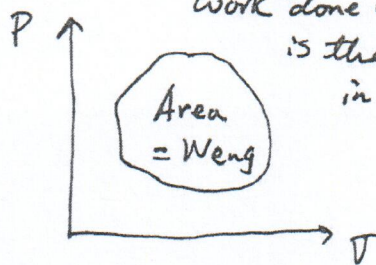Heat engines. entropy, and 2^n law of Thermodynamics

22.1 Heat engine and 2nd law of Thermodynamic

Heat engine $\equiv$ A device takes in energy by heat, operate in a cycle and expel some of its energy by means of work.

$W_{eng} \equiv$ work done by the engine

$$W_{eng} = |Q_h| - |Q_c|$$

= in a cyclic process, the work done by the engine is the enclosed area in a p-v diagram
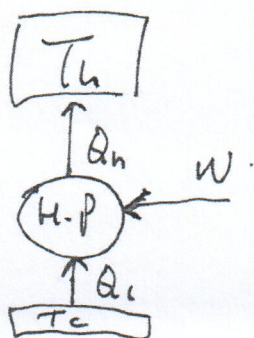
Area = W_{eng}

thermal efficiency $\equiv e = \dfrac{W_{eng}}{|Q_h|} = \dfrac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \dfrac{|Q_c|}{|Q_h|}$

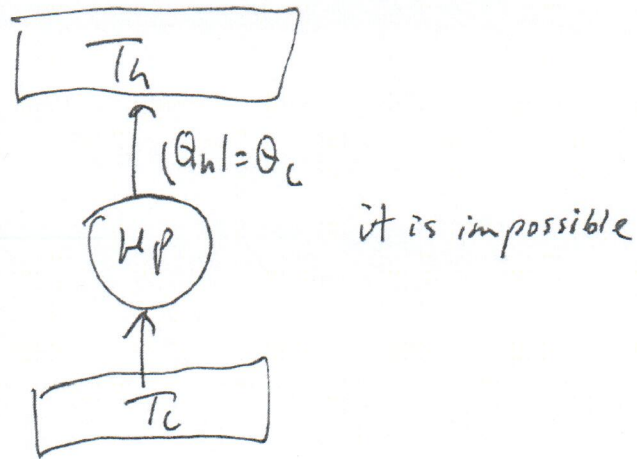Perfect engine . $Q_c = 0$, $e = 1$. impossible energy.

Kevin - Planck form of 2nd law of Thermoldynamic

— It is impossible to make a perfect engine.

22.2 Heat pump and refrigerators

heat pump = refrigerator

T_h

$|Q_h| = Q_c$

HP

it is impossible

T_c

1) ideal energy engine is impossible

2) All real processes on earth are irreversible

22.4 The Carnot Engine

Carnot's theorem — No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine between the same two reservoirs.

— All real engines are less efficient than the Carnot engine because they do not operate through a reversible cycle

reversible cycle: in a pv diagram, an engine starts from ~~good~~ an initial state and back to it initial state through the same path

P670
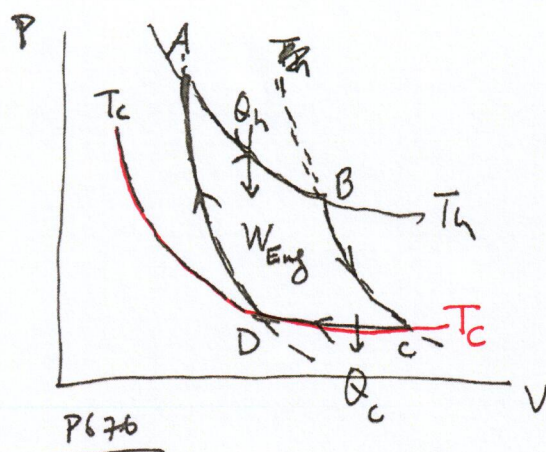
PV diagram for a Carnot engine. the net work done by the engine

$$W_{eng} = Q_h - Q_c.$$

Note Since it goes back to the initial state A.

$$\Delta E_{in} = 0$$

$$e = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

Since in a Carnot cycle, $\Delta E_{in} = 0$ $\therefore |Q_h| = |-W_{AB}|$ (process AB)

$A \rightarrow B$ $|Q_h| = |-W_{AB}| = nRT_h \ln \frac{V_B}{V_A}$ (20.13) Absorb energy

$C \rightarrow D$ $|Q_c| = |-W_{CD}| = nRT_c \ln \frac{V_C}{V_D}$ 20.14

$\therefore \frac{Q_c}{Q_h} = \frac{T_c}{T_h} \frac{\ln(V_C/V_D)}{\ln(V_A/V_B)}$

$\qquad \qquad - (1)$

But (21.20) $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$, $(P_i V_i^{\gamma} = P_f V_f^{\gamma})$

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

for process $B \to C$ and $D \to A$ (different isotherm)

$$T_h V_B^{\gamma-1} = T_c V_c^{\gamma-1} \qquad —① $$

$$T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1} \qquad —②$$

$$\frac{①}{②} \to \left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_c}{V_D}\right)^{\gamma-1}$$

or $\quad \dfrac{V_B}{V_A} = \dfrac{V_c}{V_D} \qquad — (2)$

$\therefore$, from (1) and (2)

$$\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h}$$

$$e_{Carnot} = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{|T_c|}{|T_h|} \qquad — \text{efficiency of a Carnot engine.}$$

— All Carnot engines operating between the same two temperatures have the same efficiency.

$e_c = 1$ if $T_c = 0 K$. (not exist)

$e_c = 0$ if $T_c = T_h$

Coefficiency of Performance $COP_c = \dfrac{Q_h}{W}$ (22.3)

$$COP_c = \frac{|Q_h|}{|W|} = \frac{|Q_h|}{|Q_h| - |Q_c|} = \frac{1}{1 - \frac{|Q_c|}{|Q_h|}} = \frac{1}{1 - \frac{T_c}{T_h}} = \frac{T_h}{T_h - T_c} \quad \text{(heating)}$$
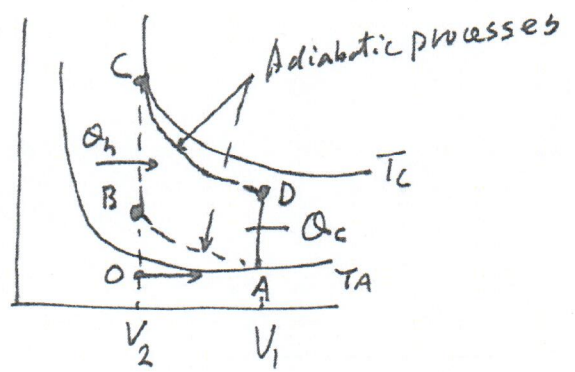
$$\therefore COP_c = \frac{T_c}{T_h - T_c} \quad (\text{cooling mode})$$

22.5 Otto Cycle

gasoline engine.

Six different processes

$$e = 1 - \frac{1}{\left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

$\frac{V_1}{V_2}$ = Compression ratio

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22.6 Entropy

22.6 Entropy

Zeroth law — temperature . T
1st law — internal energy , ΔE_{int}
2nd law — entropy S.

$\rightarrow$ thermaldynamic
Statistical mechanics
(describe th systems of atoms and
Molecules.

: Isolated systems tend toward
disorder and entropy is a
measure of disorder.

Micro states : A particular Configuration of individual
constituents

Macro States : A description of th Condition from a macroscopic
point of view. Use pressure. volume and density
of gas to describe.

The entire Universe is moving into a greater disorder state.
— the entropy of th universe increases in all real process
— Another way of describing 2nd law.

$$dS = \frac{dQ_r}{T}$$

$dQ_r \equiv$ amount of heat transferred
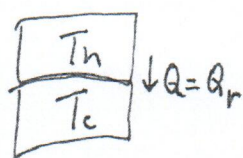when system follow a
reversible path

① depends on the ends
points only. independet
of path

$T =$ Constant because th process
is infinitesimal.

② for irreversible process.
Entropy Can be Calculated
for a reversible paths with The
Same initial and final points.

③ describe th "change" in entropy.

22.7 Entropy Changes in irreversible process

if the process is irreversible, then the total entropy
of an isolated system always increases.
in a reversible process, the total entropy of an isolated system
remains constant.

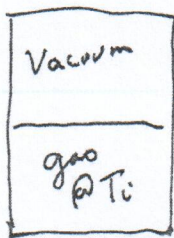① entropy change in thermal Conduction

$$\Delta S_h = \frac{-Q}{T_h}$$

$$\Delta S_c = \frac{Q}{T_c}$$

$$\text{total } \Delta S = \frac{Q}{T_c} - \frac{Q}{T_h} > 0$$

(diagram: box with T_h over T_c, $\downarrow Q = Q_r$)

② Entropy change in a free expansion

(diagram: box with Vacuum over gas @ T_i)

Adiabatic free expansion

$$V_i \rightarrow V_f$$
$$dw = 0$$
$$dQ = 0$$
$$dE_{in} = 0$$
$$\Delta T = 0 \quad T_i = T_f$$

Can't use $\Delta S = \int ds = \int_i^f \frac{dQ}{T}$ since $\frac{dQ = 0}{T_i = T_f}$

find a reversible process instead of the irreversible pocess
that has the same initial and final states
→ isothermal reversible expansion

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \frac{1}{T} \int_i^f dQ_r$$

$$dE_{in} = 0 \quad \therefore \int_i^f dQ_r = \int_i^f dw$$

$$\therefore \Delta S = \frac{1}{T} \int dw = nR \ln \frac{V_f}{V_i} \qquad (20.13)$$

$$> 0$$

for a gas expand from $V_i \rightarrow V_f$
at temperature T.

for a finite process

$$\Delta S = \int_i^f ds = \int_i^f \frac{dQ_r}{T} \quad , \quad$$ T is not a constant
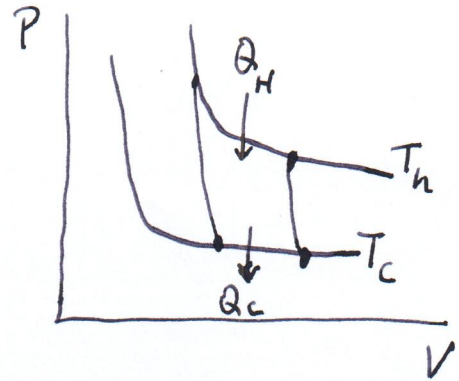dQ = positive when absorbing heat
= negative when expelling heat

① Carnot cycle:

Total entropy change in one cycle

$$\Delta S = \Delta S_h + \Delta S_c$$

$$= \frac{|Q_H|}{T_h} - \frac{|Q_c|}{T_c} \quad ,$$

But $\dfrac{|Q_c|}{|Q_H|} = \dfrac{T_c}{T_H}$ ∴ $\Delta S = 0$ for a Carnot cycle.
A perfect engine

② For a non Carnot cycle (~~irreversible~~ reversible)
cycle
for a non Carnot, but reversible cycle.
Because the entropy is a state variable, depending only on the state.
if it is reversible. Then for a closed cycle

$$\oint \frac{dQ_r}{T} = 0$$ (Since it is back to its original state, and the
state did not change)

③ for a Quasi-static reversible process, for example. ideal gas.
ideal gas, T_c. V_c.

$$dE_{int} = dQ_r + dW \quad ,$$ Here dW is the work done on
the gas. (or on the system)

$$dQ_r = dE_{int} - dW$$

$$= dE_{int} - p\,dV$$

$$= dE_{int} - nRT \frac{dV}{V}$$

$$= n\,C_v\,dT - nRT\frac{dV}{V}$$

⇒ $PV = nRT$
⇒ $P = nRT\dfrac{1}{V}$

$$∴ \Delta S = \int_i^f \frac{dQ_r}{T} = \int_{T_c}^{T_f} nC_v \frac{dT}{T} - nRT \int_{V_c}^{V_f} \frac{dV}{V}$$

→ ΔS depends only on
the initial and final
states of the system.

$$= nC_v \ln\left(\frac{T_f}{T_c}\right) - nR \ln\left(\frac{V_f}{V_c}\right)$$

③ Entropy Change in Calorimetric process

$T_h > T_c$

$Q_c = - Q_{hot}$

$m_1 c_1 \Delta T_c = - m_2 c_2 \Delta T_h$
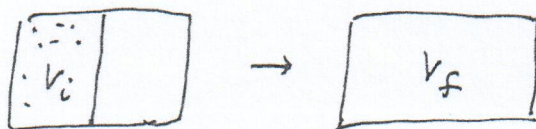
$m_1 c_1 (T_f - T_c) = - m_2 c_2 (T_f - T_h)$

$$T_f = \frac{m_1 c_1 T_c + m_2 c_2 T_h}{m_1 c_1 + m_2 c_2}$$

$$\Delta S = \int_1 \frac{d Q_c}{T} + \int_2 \frac{d Q_h}{T} = m_1 c_1 \int_{T_c}^{T_f} \frac{dT}{T} + m_2 c_2 \int_{T_h}^{T_f} \frac{dT}{T}$$

$$= m_1 c_1 \ln \frac{T_f}{T_c} + m_2 c_2 \ln \frac{T_f}{T_h}$$

$$> 0$$

22.8   Entropy on a Macroscopic Scale

$w_i = \dfrac{V_i}{V_m} \equiv$ the total number of possible locations of a single molecules. (very large number)

= number of ways that molecules can be placed in the volume

The number of ways locating N molecules is $W_i = w_i^N$

$$W_i = \left(\frac{V_i}{V_m} \right)^N = w_i^N$$

$$W_f = \left(\frac{V_f}{V_m} \right)^N = w_f^N$$

$$\frac{W_f}{W_i} = \frac{\left(\frac{V_f}{V_m}\right)^N}{\left(\frac{V_i}{V_m}\right)^N} = \left(\frac{V_f}{V_i}\right)^N$$

$$\rightarrow k_B \ln\left(\frac{W_f}{W_i}\right) = k_B \ln\left(\frac{V_f}{V_i}\right)^N = n N_A k_B \ln\left(\frac{V_f}{V_i}\right)$$

$$\rightarrow k_B \ln W_f - k_B \ln W_i = n R \ln\left(\frac{V_f}{V_i}\right)$$

$$(22.13) \quad S_f - S_i = n R \ln\left(\frac{V_f}{V_i}\right)$$

$$\therefore S_f = k_B \ln W_f$$
$$S_i = k_B \ln W_i$$

$$\boxed{S \equiv k_B \ln W}$$

entropy is a measure of
disorder