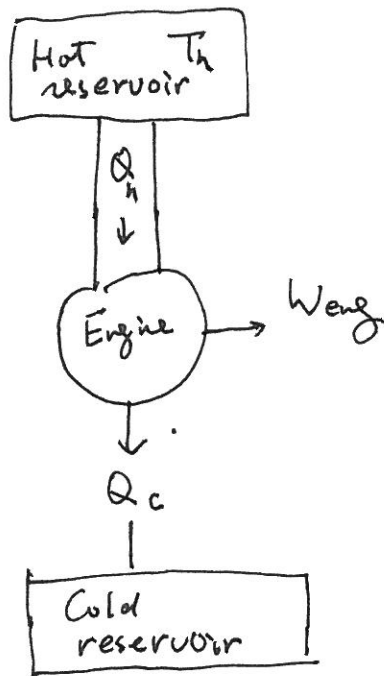Chap 22.

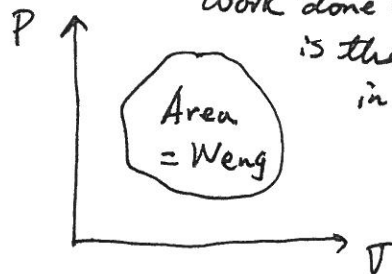Heat engines. entropy, and 2nd law of thermodynamics

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

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

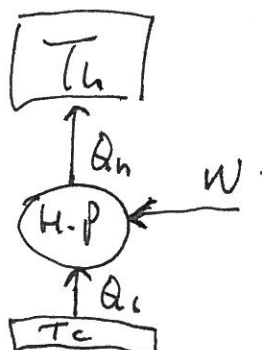= in a cyclic process, the work done by the engine is the enclosed area in a p-v diagram

Area = W_{eng}

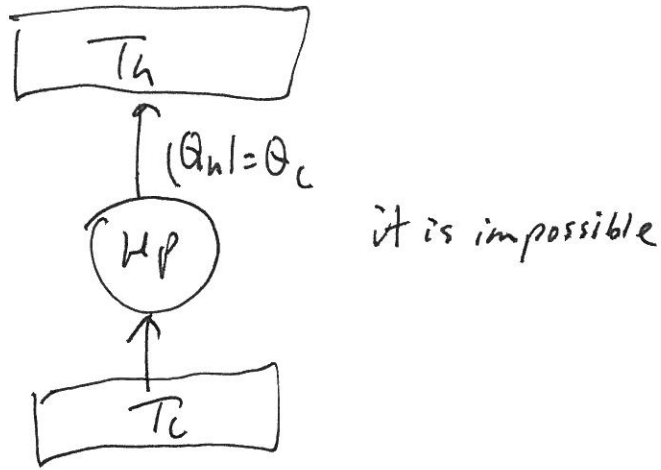thermal efficiency $\equiv e = \dfrac{W_{eng}}{|Q_h|} = \dfrac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \dfrac{|Q_c|}{|Q_h|}$

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 ~~an~~ an initial state and back to it initial state through the same path

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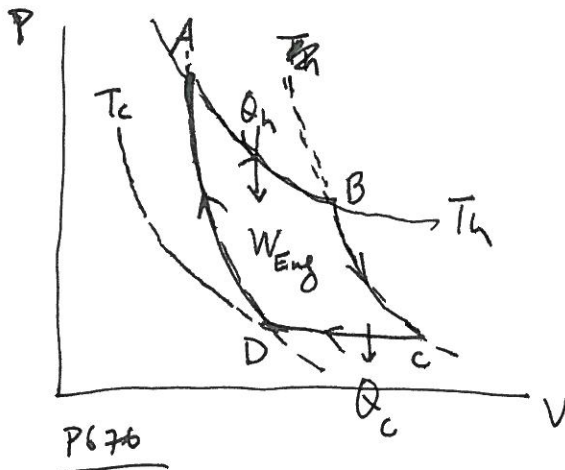
PV diagram for a Carnot engine. the net work done by the engine

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

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 . $\Delta E_{in} = 0$ ∴ $|Q_h| = |-W_{AB}|$ (process AB)

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

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

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

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

— (1)

(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 $\dfrac{V_B}{V_A} = \dfrac{V_c}{V_D} \qquad -(2)$

$\therefore$ 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 $T_c = T_h$

Coefficient of Performance $CoP_c = \dfrac{Q_h}{W}$ \qquad (22.3)

$$CoP_c = \frac{|Q_h|}{|W|} = \frac{|Q_h|}{|Q_h| - |Q_c|} = \frac{1}{1 - \frac{|Q_c|}{|Q_h|}} = \frac{1}{1 - \frac{T_c}{T_h}} = \frac{T_h}{T_h - T_c} \quad (\text{heating})$$

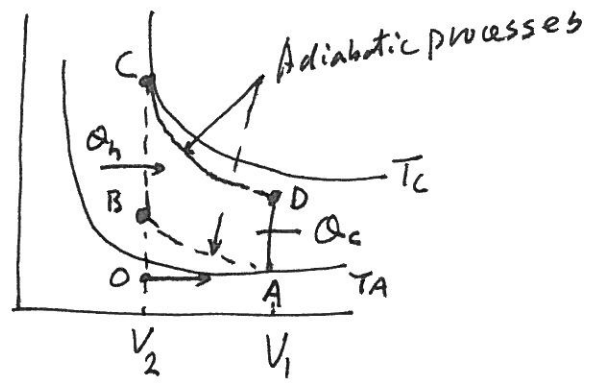$\therefore CoP_c = \dfrac{T_c}{T_h - T_c} \quad (\text{cooling mode})$

22.5 Otto cycle

gasoline engine.

six different processes

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

$\dfrac{V_1}{V_2} =$ 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.

      $\rightarrow$ thermodynamic
      statistical mechanics
        (describe the 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 the 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 the 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. independent of path

$T \equiv$ constant because the process is infinitesimal.

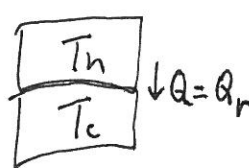② for irreversible process. Entropy can be calculated for a reversible paths with the same initial and final points.

③ describe the "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
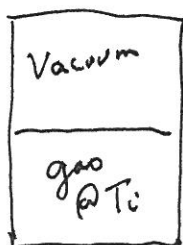remains Constant.

① entropy change in thermal Conduction

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

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

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

② Entropy change in a free expansion

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 $\Delta S = \int_i^f dS = \int_i^f \frac{dQ}{T}$ since $\frac{dQ = 0}{T_i = T_f}$

find a reversible process instead of the irreversible process.
~~that~~ has the same initial and final States

→ isothermal reversible expansion

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

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

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

> 0

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

for a finite process
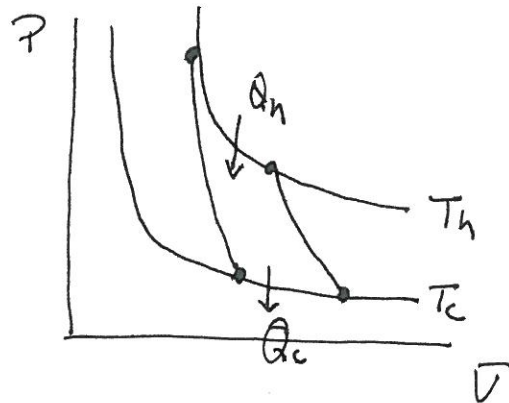
$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

T is not a Constant.
dQ = positive when absorbing heat
= negative when expelling heat

① Carnot cycle:

Total change in entropy for one cycle

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

$$= \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T}$$

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

∴ $\Delta S = 0$ for a Carnot cycle

② Non Carnot cycle — A reversible cycle

$$\Delta S = 0$$

$$\rightarrow \oint \frac{dQ_r}{T} = 0 \qquad \oint \equiv \text{the integration over a closed path.}$$

③ Consider a Quasi-Static, reversible process for an ideal gas, T_i, V_i.

$(-)$ by
$(+)$ on

dW = Work done on the gas

$$= + PdV$$

$$dE_{int} = dQ_r \mp dW$$

$$dQ_r = dE_{int} \pm dW$$

$~~PdV = nRdT$

$~~PV = nRT$

$$= dE_{int} + PdV$$

$~~P = \frac{nRT}{V}$

$$= nC_V dT + nRT \frac{dV}{V}$$

$$\frac{dQ_r}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$\Delta S = \int_i^f \frac{dQ_r}{T} = nC_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

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

③ Entropy Change in Calorimetric process

$m_1 c_1 \Delta T_c = -m_2 c_2 \Delta T_h$

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

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

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

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

$$> 0$$

22.8   Entropy on a Macroscopic Scale

$\omega_i = \frac{V_i}{V_m} \equiv$ 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 $W_i = \omega_i^N$

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

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

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

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

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

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

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

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

entropy is a measure of disorder