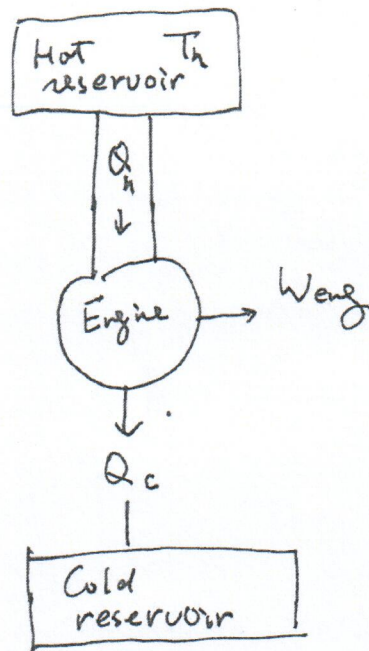


Chap 22. (Chapter 21 for 10ed. of Serway) 22-1
 updated
 Heat engines, entropy, and 2nd law of thermodynamics

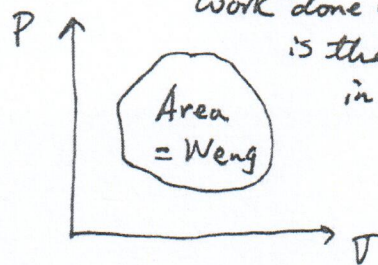
22.1 Heat engine and 2nd law of thermodynamics

Heat engine $\equiv$ A device takes in energy by heat, operates in a cycle and expels 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



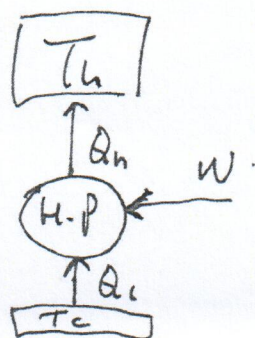
$$\text{thermal efficiency} \equiv e = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

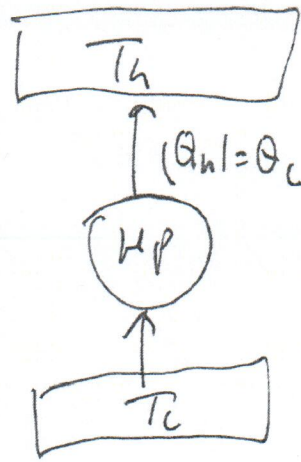
Perfect engine: $Q_c = 0$, $e = 1$. impossible energy.

Kein-Planck form of 2nd law of thermodynamics
 — It is impossible to make a perfect engine.

22.2 Heat pump and refrigerators

heat pump = refrigerator





it is impossible

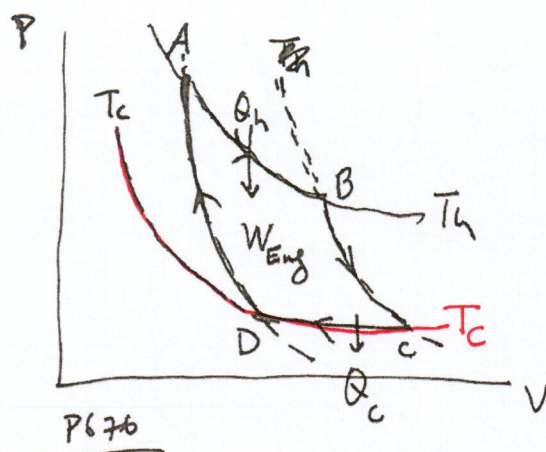
- 1) ideal ~~eng~~ engine is impossible
- 2) All real processes on earth are irreversible

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 initial state and back to its initial state through the same path



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

$$W_{\text{eng}} = Q_h - Q_c$$

Note Since it goes back to its initial state A.

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

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

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

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

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

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

— (1)

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

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

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

$$T_h V_B^{\gamma-1} = T_c V_c^{\gamma-1} \quad \text{--- (1)}$$

$$T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1} \quad \text{--- (2)}$$

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

$$\text{or } \frac{V_B}{V_A} = \frac{V_c}{V_D} \quad \text{--- (2)}$$

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

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

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

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

$$e_c = 1 \text{ if } T_c = 0 \text{ K. (not exist)}$$

$$e_c = 0 \text{ if } T_c = T_h$$

$$\text{Coefficient of performance } \text{COP}_c = \frac{Q_h}{W} \quad (22.3)$$

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

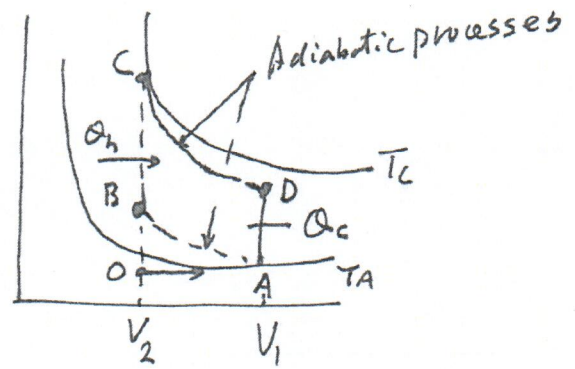
$$\therefore \text{COP}_c = \frac{T_c}{T_h - T_c} \quad (\text{cooling mode})$$

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
22.6 Entropy

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22.6 Entropy

Zeroth law - temperature . T

1st law - internal energy , ΔE_{int}

2nd law - entropy S .

→ 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 end 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.

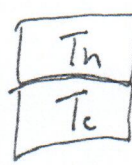
- ③ describe the "change" in entropy.

22.7 Entropy Change 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

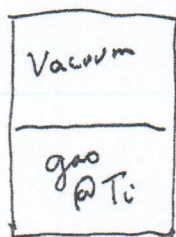


$$\Delta S_h = -\frac{Q}{T_h}$$

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

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

② Entropy change in a free expansion



Adiabatic free expansion

$$V_i \rightarrow V_f$$

$$dw = 0$$

$$dQ = 0$$

$$dE_{\text{int}} = 0$$

$$\Delta T = 0 \quad T_i = T_f$$

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

find a reversible process instead of the irreversible process that has the same initial and final states

→ isothermal reversible expansion

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

$$dE_{\text{int}} = 0 \therefore \int_i^f dQ_r = \int_i^f dw$$

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

$$> 0$$

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

for a finite process

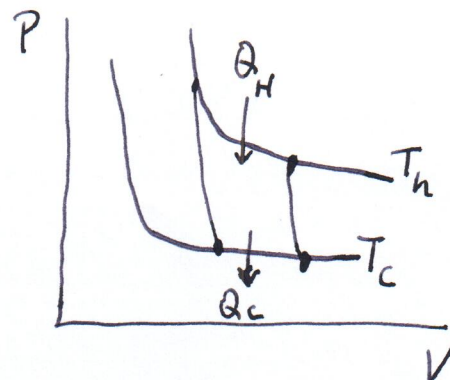
$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}, \quad T \text{ is not a constant}$$

$dQ = \text{positive when absorbing heat}$
 $= \text{negative when expelling heat}$

① Carnot cycle:

Total entropy change in one cycle

$$\begin{aligned} \Delta S &= \Delta S_h + \Delta S_c \\ &= \frac{|Q_H|}{T_h} - \frac{|Q_C|}{T_c} \end{aligned}$$



But $\frac{|Q_C|}{|Q_H|} = \frac{T_c}{T_h} \therefore \Delta S = 0$ for a Carnot cycle.
 A perfect engine

② For a non Carnot cycle (~~reversible~~ 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

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

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

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

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

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

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

$$= nC_v dT - nRT \frac{dV}{V}$$

$$\Rightarrow PV = nRT$$

$$\rightarrow P = nRT \frac{1}{V}$$

$$\begin{aligned} \therefore \Delta S &= \int_i^f \frac{dQ_r}{T} = \int_{T_c}^{T_f} nC_v \frac{dT}{T} - nRT \int_{V_c}^{V_f} \frac{dV}{V} \\ &= nC_v \ln\left(\frac{T_f}{T_c}\right) - nR \ln\left(\frac{V_f}{V_c}\right) \end{aligned}$$

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

(3) Entropy change in Calorimetric process

$$\begin{array}{cc} \boxed{m_1} & \boxed{m_2} \\ c_1 & c_2 \\ T_c & T_h \end{array} \quad T_h > T_c$$

$$Q_c = -Q_{hot}$$

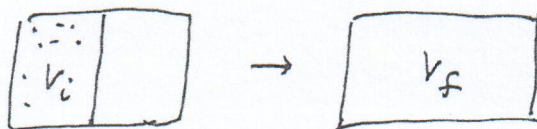
$$m_1 c_1 \Delta T_c = -m_2 c_2 \Delta T_h$$

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

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

$$\begin{aligned} \Delta S &= \int_1 \frac{dQ_c}{T} + \int_2 \frac{dQ_h}{T} = m_1 c_1 \int_{T_c}^{T_f} \frac{dT}{T} + m_2 c_2 \int_{T_h}^{T_f} \frac{dT}{T} \\ &= m_1 c_1 \ln \frac{T_f}{T_c} + m_2 c_2 \ln \frac{T_f}{T_h} \\ &> 0 \end{aligned}$$

22.8 Entropy on a microscopic scale



$$\begin{aligned} \omega_i &= \frac{V_i}{V_m} \equiv \text{the total number of possible locations of a single molecule. (very large number)} \\ &= \text{number of ways that molecules can be placed in the volume} \end{aligned}$$

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

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

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

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

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

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

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

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

$$S_i = k_B \ln W_i$$

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

entropy is a measure of disorder