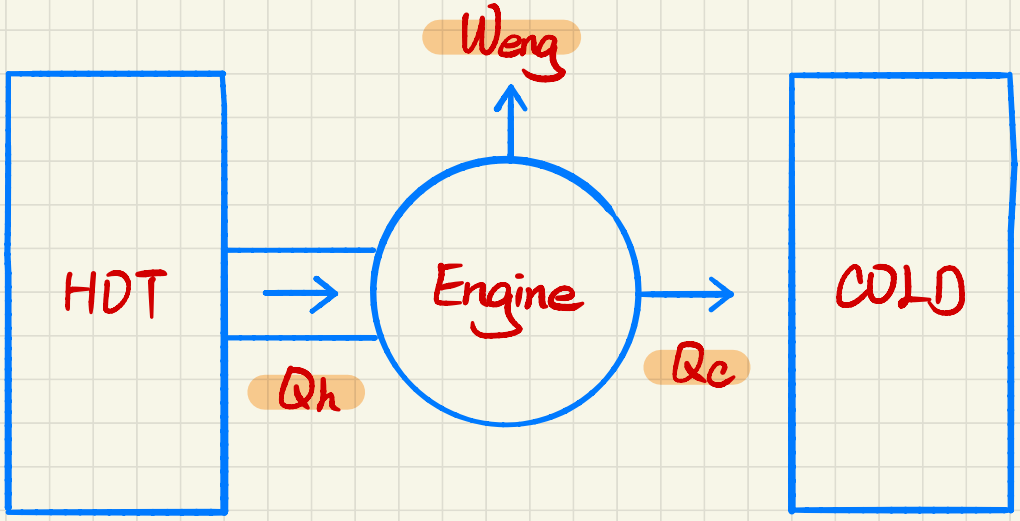
CHAPTER 22 :

heat engines, entropy and 2nd law of thermodynamics

Sector 1 :

Definition of " Heat Engine " :

A device takes in energy by heat, operates in a cycle and expel some of its energy by means of work.

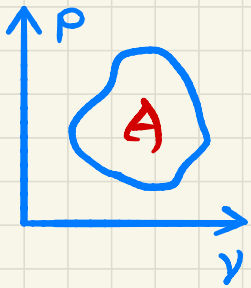


Definition of " W_{eng} " :

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



Definition of " Thermal Efficiency " :

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

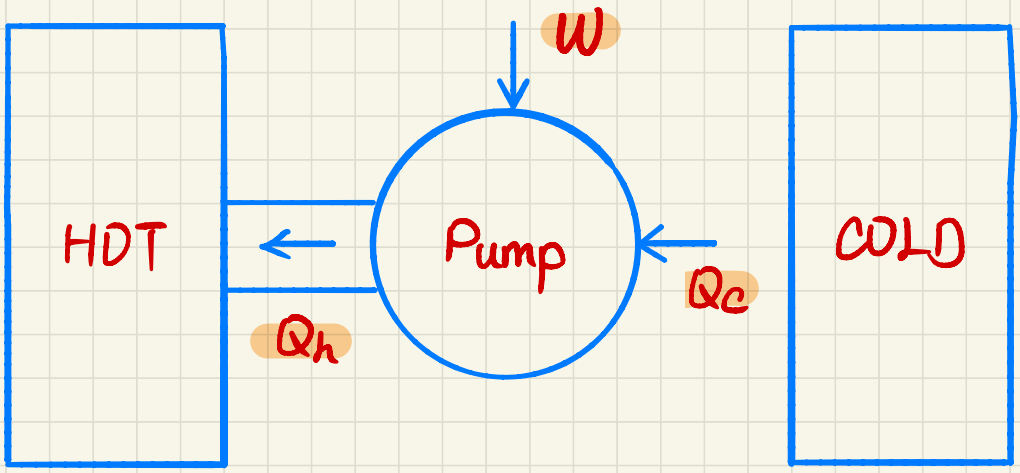
Perfect Engine : $Q_c = 0$, $e = 1$

Kevin - Plank form the 2nd law of thermodynamic

⇒ Impossible to make a perfect engine.

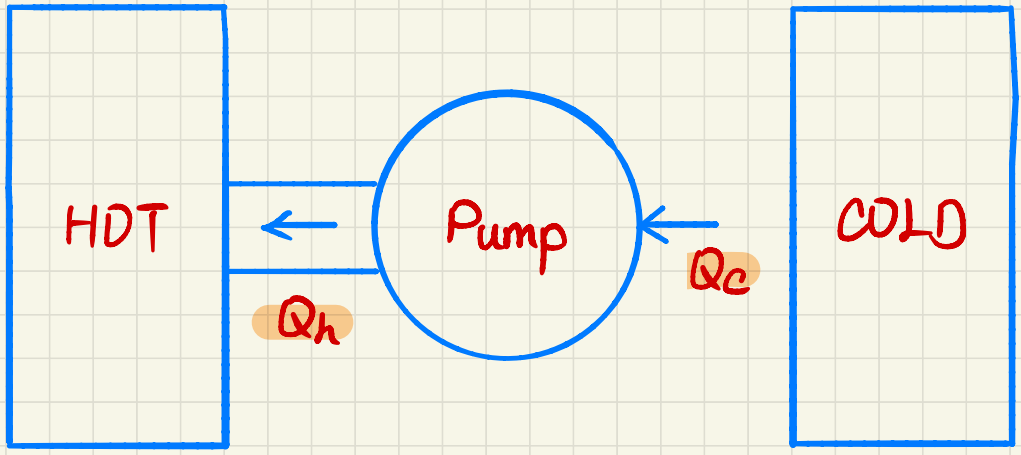
Sector 2 :

Heat Pump ⇒ Refrigerator



Ideal Engine ⇒ Impossible

All heat process on earth are irreversible.



Sector 3 : Carnot Engine

Carnot's Theorum :

No heat engine operating between two energy reservoirs can be more efficient than a carnot engine between the same two reservoirs.

All heat engines are less efficient than the carnot engine because do not operate through a reversible cycle.

Reversible cycle :

In a P-V diagram, an engine starts from an initial status and back to the initial state through the same path.

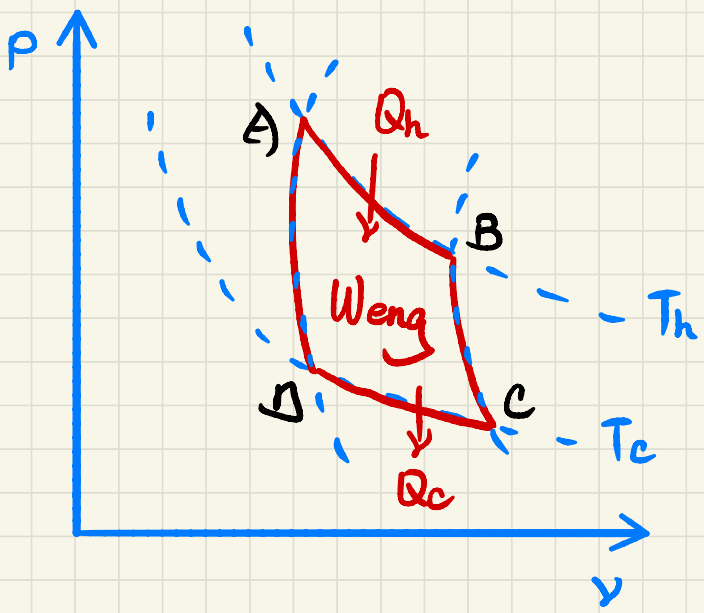
P - V diagram for a Carnot engine :

The net work done by the engine :

$$W_{eng} = Q_h - Q_c \quad *$$

Since it goes back to the initial state :

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



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

In a carnot engine :

$$\begin{cases} W = nRT\ln\left(\frac{V_i}{V_f}\right) \\ P_i V_i^{\gamma} = P_f V_f^{\gamma} \end{cases}$$

After the derivation

$$\Rightarrow e_{carnot} = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{|T_c|}{|T_h|}$$

(Efficiency of a carnot engine)

All Carnot engines operating between the same two temperature have the same efficiency.

$$\begin{cases} \text{if } T_c = 0 \text{ , } e_c = 1 \\ \text{if } T_c = T_h \text{ , } e_c = 0 \end{cases}$$

Not possible

Coefficiency of Performance = $\frac{Q_h}{W}$:

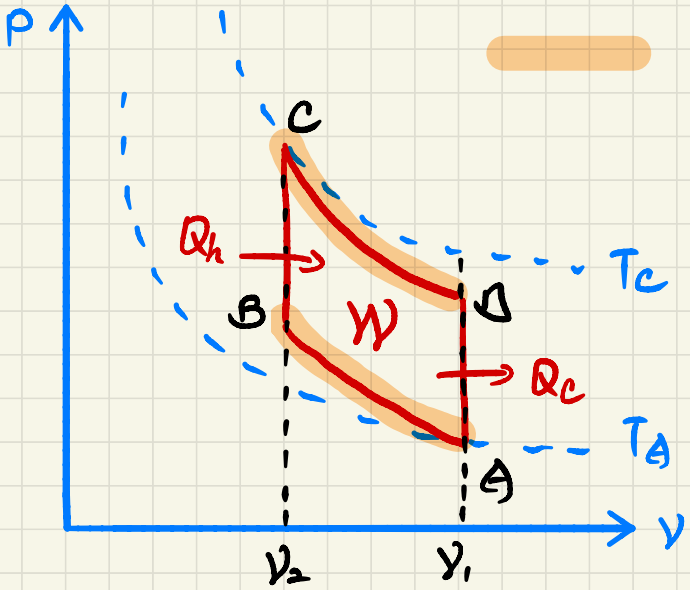
$$CoP_c = \frac{|Q_h|}{|W|} = \frac{|Q_h|}{|Q_h| - |Q_c|}$$ Heating

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

$$\therefore CoP_c = \frac{T_c}{T_h - T_c}$$ Cooling

Sector 4 : Otto Cycle

Gasoline engine



⇒ Adiabatic Process

Six Different Process

$$e_{otto} = 1 - \frac{1}{(\frac{V_1}{V_2})^{r-1}}$$

($\frac{V_1}{V_2}$ ⇒ Compression Ratio)

Sector 5 : Entropy

- Zeroth Law : Temperature , T
- 1st Law : Internal Energy , ΔE_{int}
- 2nd Law : Entropy , S

⇒ Thermodynamics
Statistical Mechanics

Describe the system 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 discription of the condition from a macroscopic point of view.

Use pressure, volume and density of gas to describle.

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 :

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

Definition of dQ_r :

Amount of heat transferred into system following a reversible path.

Definition of T :

Constant because the process is " infinitestimal ".

Point of the concept :

1. Depends on the end point
   (Independent to the path)
2. Entropy can be calculated for a reversible path with the same initial and final point.
   (For irreversible process)
3. Describe the " change " in entropy.

Part

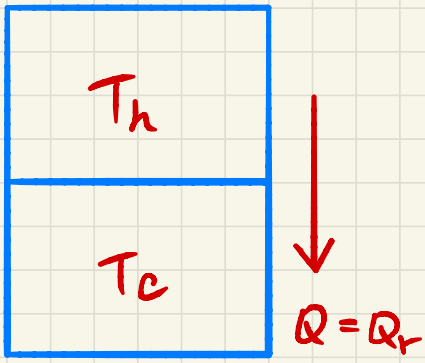
Whole

Sector 6 :

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 constants.

1. Entropy change in thermal conduction :

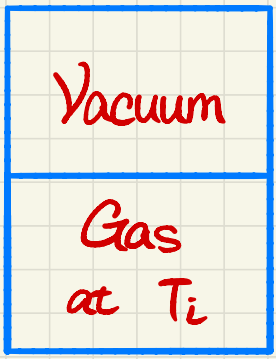


$$\Delta S_h = \left(-\frac{Q}{T_h}\right)$$

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

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

2. Entropy change is a free expansion :



Adiabatic free expansion

$$V_i \longrightarrow V_f$$

$$dW = 0 \quad , \quad dQ = 0$$

$$dE_{in} = 0 \quad , \quad \Delta T = 0$$

$$(T_i = T_f)$$

Can't use $\Delta S = \int_i^f dS = \int_i^f \frac{dQ}{T}$

(Since $dQ = 0$, $T_i = T_f$)

Find a reversible process instead of the irreversible process, which has the same initial and final states.

⇒ Isothermal reversible expansion

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

$$\Rightarrow dE_{in} = 0 \quad \therefore \int_i^f dQ_r = \int_i^f dW \ *$$

$$\therefore \Delta S = \frac{1}{T}\int dW = nR \ln \frac{V_f}{V_i} > 0$$

(For a gas expend from $V_i \rightarrow V_f$ at temperature T)

For a limited process :

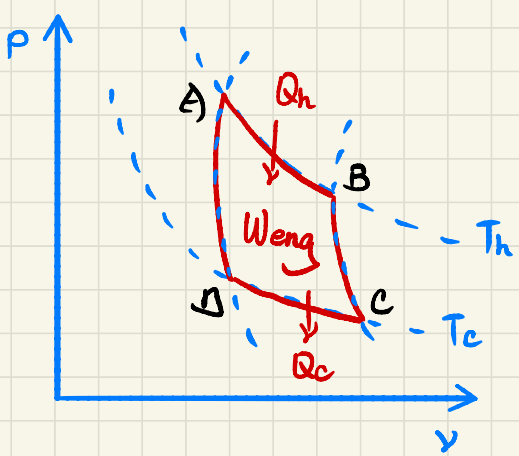
$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

(T is not a constant.

dQ = positive when absorbing heat

= negative when expeling heat)

1. Carnot Cycle :



Total change in entropy for the cycle :

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

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

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

$\Rightarrow \Delta S = 0$ for a carnot engine.

2. Non - Carnot Cycle :

A reversible cycle

$$\Delta S = 0 \Rightarrow \oint \frac{dQ_r}{T} = 0$$

⇒ The integration over a chosed path

3. Consider a quasistatic, reversible process for an ideal gas, T_i, V_i :

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

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

$$= dE_{int} - pdV$$

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

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

The work done on the gas :

⇒ $PV = nRT$

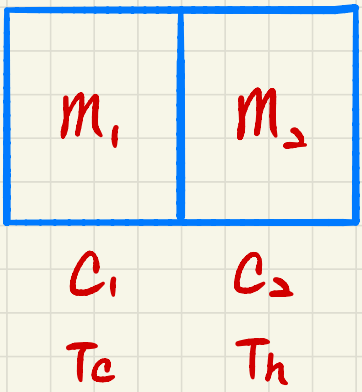
⇒ $P = nRT\frac{1}{V}$

$$\therefore \Delta S = \int_i^f \frac{dQ_r}{T} = \int_{T_i}^{T_f} nC_V \frac{dT}{T} - nRT\int_{V_i}^{V_f}\frac{dV}{V}$$

$$= nC_V \ln\left(\frac{T_f}{T_i}\right)^{T_i} - nR\ln\left(\frac{V_f}{V_i}\right)$$

⇒ ΔS depends only on the initial and final state of the system.

4. Entropy change in calorimetric process :



$T_h > T_c$

$Q_c = (-Q_h)$

$$m_1 C_1 \Delta T_c = (-m_2 C_2 \Delta T_h)$$

$$m_1 C_1 (T_f - T_c) = -m_2 C_2 (T_f - T_c)$$

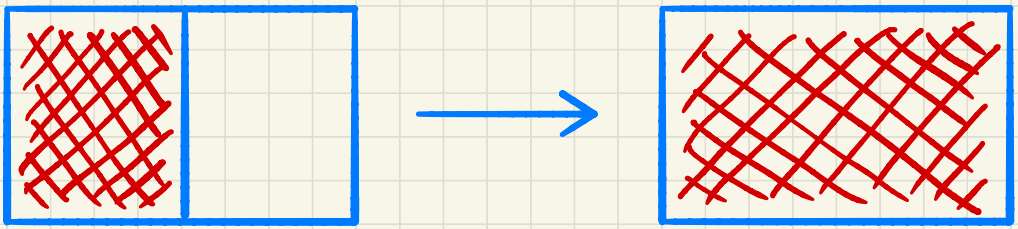
$$T_f = \frac{m_1 C_1 T_c + m_2 C_2 T_h}{m_1 C_1 + m_2 C_2}$$

$$\Delta S = \int \frac{dQ_c}{T} + \int \frac{dQ_h}{T}$$

$$= m_1 C_1 \int_{T_c}^{T_f} \frac{dT}{T} + m_2 C_2 \int_{T_c}^{T_f} \frac{dT}{T}$$

$$= m_1 C_1 \ln \frac{T_f}{T_c} + m_2 C_2 \ln \frac{T_f}{T_h} > 0$$

Sector 7 :



$W_i = \frac{V_i}{V_m}$ (The total number of possible locations of a single molecules)

⇒ Number of ways that molecules can be placed in the volume.

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

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

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

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

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

$$= nN_A k_B \ln\left(\frac{V_f}{V_i}\right)$$

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

$$S_f - S_i = nR \ln\left(\frac{V_f}{V_i}\right)$$

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

$$S_i = k_B \ln W_i$$

$$S \equiv k_B \ln W$$

Entropy is a measure of disorder.