

Chapter 22 Heat Engines, Entropy and the Second Law of Thermodynamics

First law states that energy is conserved.

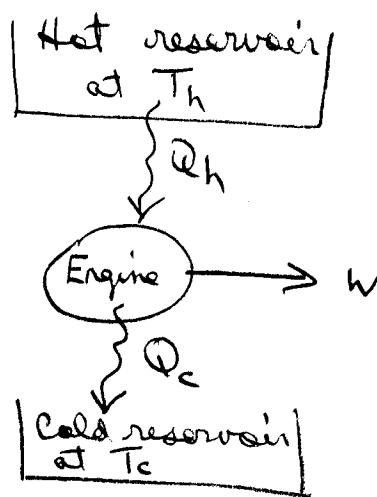
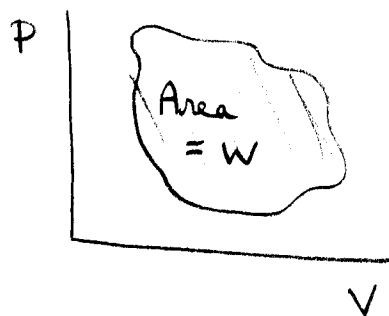
Second law establishes which processes can and cannot occur.

22.1 Heat Engines and the Second Law of Thermodynamics

Heat engine:

- Working substance

- cyclic process $\Rightarrow \Delta U = 0 \Rightarrow W = Q_h - Q_c$



Thermal Efficiency, $e \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$

Typically, $e \sim 20 \rightarrow 40\%$ in engines.

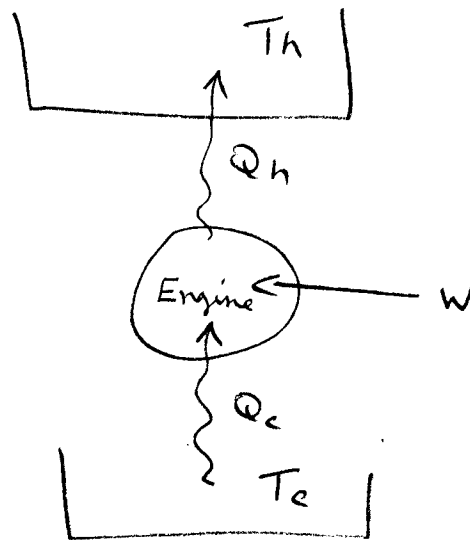
2nd Law: It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of thermal energy from a reservoir and the performance of an equal amount of work. (Kelvin-Planck)

- in short: $Q_c \neq 0$

Refrigerators and Heat Pumps

These are heat engines in reverse.

Must do work, W , to cause thermal energy to flow from cold reservoir to hot reservoir. (Clausius)

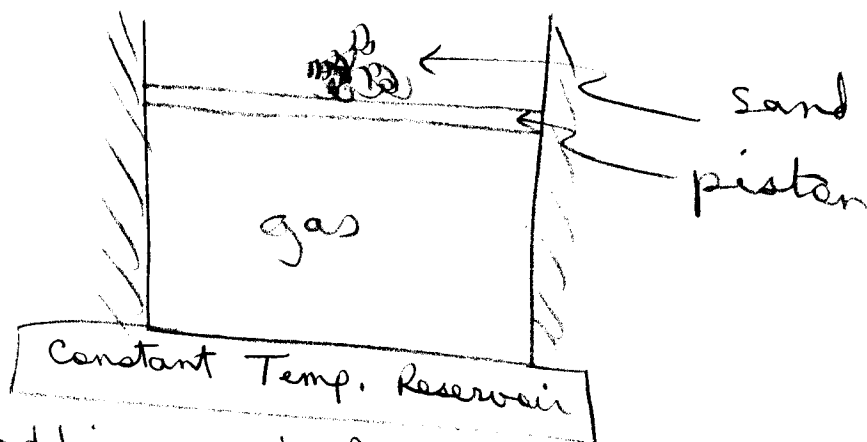


22.2 Reversible and Irreversible Processes

Reversible Process: one that can be performed so that, at its conclusion, both the system and its surroundings have been returned to their exact initial conditions.

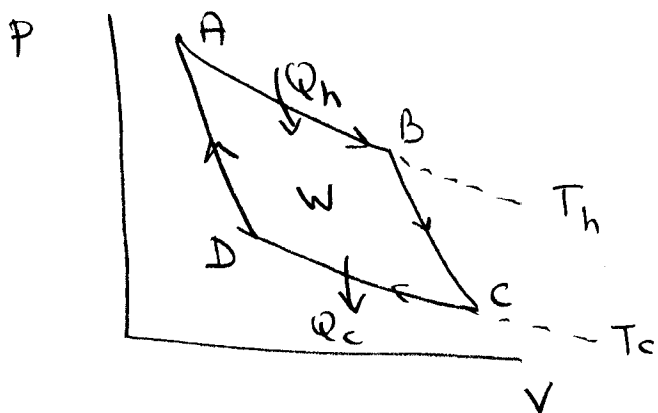
Irreversible Process: one that does not satisfy the above.

All real processes are irreversible but in some cases we can approximate a reversible process by minimizing dissipation effects such as friction.



slowly adding grains of sand causes a reversible compression of the gas - i.e. the system looks reversible but the surroundings are not.

22.3 The Carnot Engine

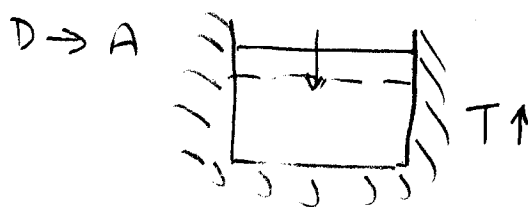
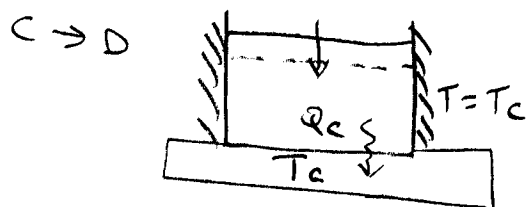
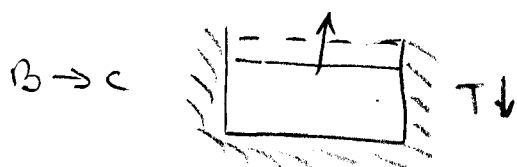
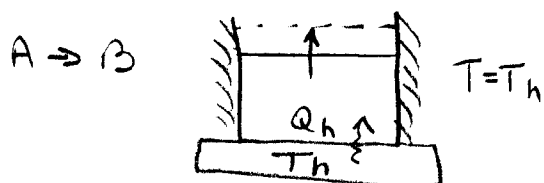


$A \rightarrow B$ Isothermal expansion at T_h
 $Q = Q_h$ (= heat added)

$B \rightarrow C$ Adiabatic expansion
 $Q = 0$

$C \rightarrow D$ Isothermal compression at T_c
 $Q = Q_c$ (= heat rejected)

$D \rightarrow A$ Adiabatic compression
 $Q = 0$



A → BT constant $\therefore \Delta U_{\text{gas}} = 0$

$$\therefore Q_h = W_{AB} = nRT_h \ln(V_B/V_A)$$

C → D

Similar to A → B

$$\therefore Q_c = -W_{CD} = nRT_c \ln(V_c/V_D)$$

B → C

Adiabatic, quasi-static expansion.

$$\therefore PV^\gamma = \text{constant}$$

$$\& PV = nRT$$

$$\Rightarrow TV^{\gamma-1} = \text{constant}$$

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

D → A

Similar to B → C

$$\therefore T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

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

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

$$\therefore e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \leftarrow \text{for Carnot Cycle}$$

from Serway Chapter 21:

$$du = nC_v dT = \underbrace{-PdV}_{-W}$$

but $PV = nRT$ if ideal gas

$$\therefore PdV + VdP = nRdT \leftarrow$$

$$\therefore PdV + VdP = -\frac{R}{C_v} PdV$$

$$\text{Now } R = C_p - C_v$$

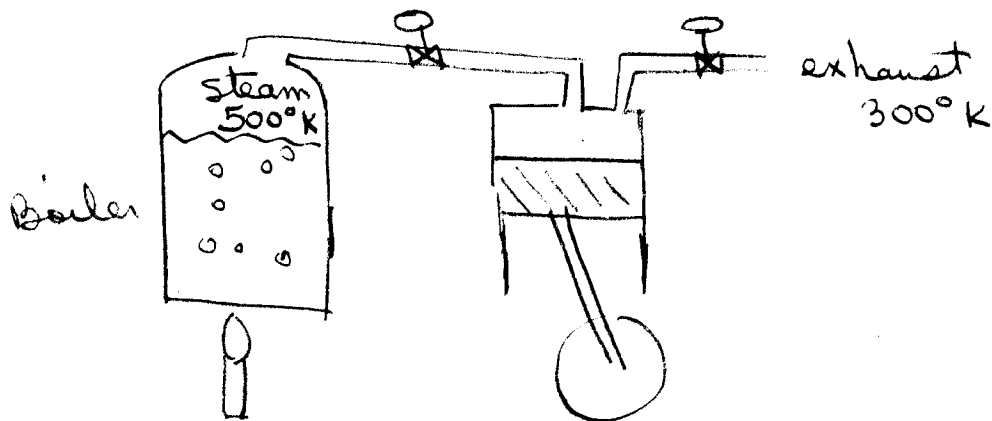
$$\therefore \frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

$$\text{where } \gamma = C_p/C_v$$

$$\Rightarrow \ln P + \gamma \ln V = \text{constant}$$

$$\therefore PV^\gamma = \text{constant.}$$

Example: The Steam Engine



Find maximum efficiency.

$$e_{\text{carnot}} = 1 - \frac{T_c}{T_h} = 1 - \frac{300\text{K}}{500\text{K}} = 0.4 \text{ or } \underline{40\%}$$

Find W_{max} if $Q_h = 200 \text{ J}$.

$$e = 1 - \frac{Q_c}{Q_h} = \frac{W}{Q_h} = 0.4 \quad \therefore \quad W = 0.4 \times 200 \text{ J} = \underline{80 \text{ J}}$$

Example: The Carnot Efficiency

Gas engine, $e = 30\%$, $T_c = 300\text{K}$, $T_h = ?$
(assume Carnot)

$$e = 0.3 = 1 - \frac{T_c}{T_h} \quad \therefore \quad T_h = \frac{T_c}{1-e} = \frac{300}{.7} = \underline{\underline{492 \text{ K}}}$$

If $Q_h = 837 \text{ J}$ find W .

$$W = e Q_h = 0.3 \times 837 \text{ J} = \underline{\underline{251 \text{ J}}}$$

22.4 The Absolute Temperature Scale

We can use the Carnot cycle as a means of measuring temperature.

Choose a reference temperature: 273.16 K
 (triple point of water, i.e. the temp. at which water in vapour, liquid and ice coexist -
 $T = 0.01^\circ\text{C}$, $P = 4.58 \text{ mm. Hg}$)

For Carnot cycle we showed that

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

- Run a substance through the Carnot cycle wherein $T_c = 273.16 \text{ K}$.
- Measure $Q_c + Q_h$.
- Infer T_h from $T_h = (273.16 \text{ K}) \times \frac{Q_h}{Q_c}$

22.5 The Gasoline Engine

Otto cycle

$O \rightarrow A$ Intake stroke
Vol increases from
 $V_2 \rightarrow V_1$

$A \rightarrow B$ Compression stroke

Adiabatic

$V_1 \rightarrow V_2$, $T_A \rightarrow T_B$ (T increase)

Work of compression = area under AB

$B \rightarrow C$ Combustion, Q_h added

$V \sim$ constant, $P \uparrow$, $T \uparrow$, $W = 0$

$C \rightarrow D$ Power stroke

Adiabatic expansion, $V_2 \rightarrow V_1$

$T \downarrow$, $T_c \rightarrow T_0$

Work of expansion = area under CD

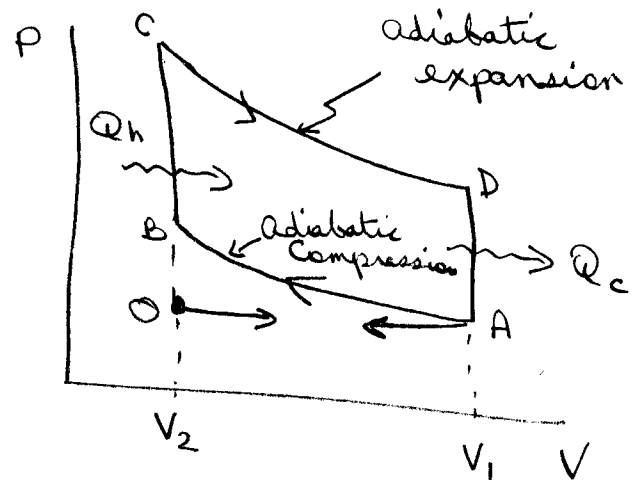
$D \rightarrow A$ Exhaust valves open

$P \downarrow$, V constant, $W = 0$, Q_c removed

$A \rightarrow O$ Exhaust stroke

Residual gas removal

$V \downarrow$, $V_1 \rightarrow V_2$



Example: Efficiency of the Otto Cycle

Assume ideal gas. $\Delta U = 0$ for a cycle.

$$\therefore W = Q_h - Q_c$$

$$Q_h = n C_v (T_c - T_b) \quad (\text{constant volume heat addition})$$

$$Q_c = n C_v (T_D - T_A) \quad (\text{constant volume heat removal})$$

$$\therefore e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{(T_D - T_A)}{(T_c - T_b)}$$

Now since $A \rightarrow B$ + $C \rightarrow D$ are adiabatic:

$$T_A V_1^{\delta-1} = T_B V_2^{\delta-1} \quad , \quad \delta = C_p/C_v \approx 1.4$$

and $T_D V_1^{\delta-1} = T_c V_2^{\delta-1}$

$$\begin{aligned} \therefore \frac{T_D - T_A}{T_c - T_b} &= \frac{T_c (V_2/V_1)^{\delta-1} - T_B (V_2/V_1)^{\delta-1}}{T_D - T_B} \\ &= (V_2/V_1)^{\delta-1} \end{aligned}$$

$$\therefore e = 1 - \frac{1}{(V_1/V_2)^{\delta-1}}$$

V_1/V_2 is called the compression ratio.

If $V_1/V_2 = 8$ (typical)
then $e = 56\%$

$e \uparrow$ as $V_1/V_2 \uparrow$

Actual is $\sim 20\%$ due to friction, heat losses + incomplete combustion.

In terms of temperatures:

$$T_A V_1^{\gamma-1} = T_B V_2^{\gamma-1}$$

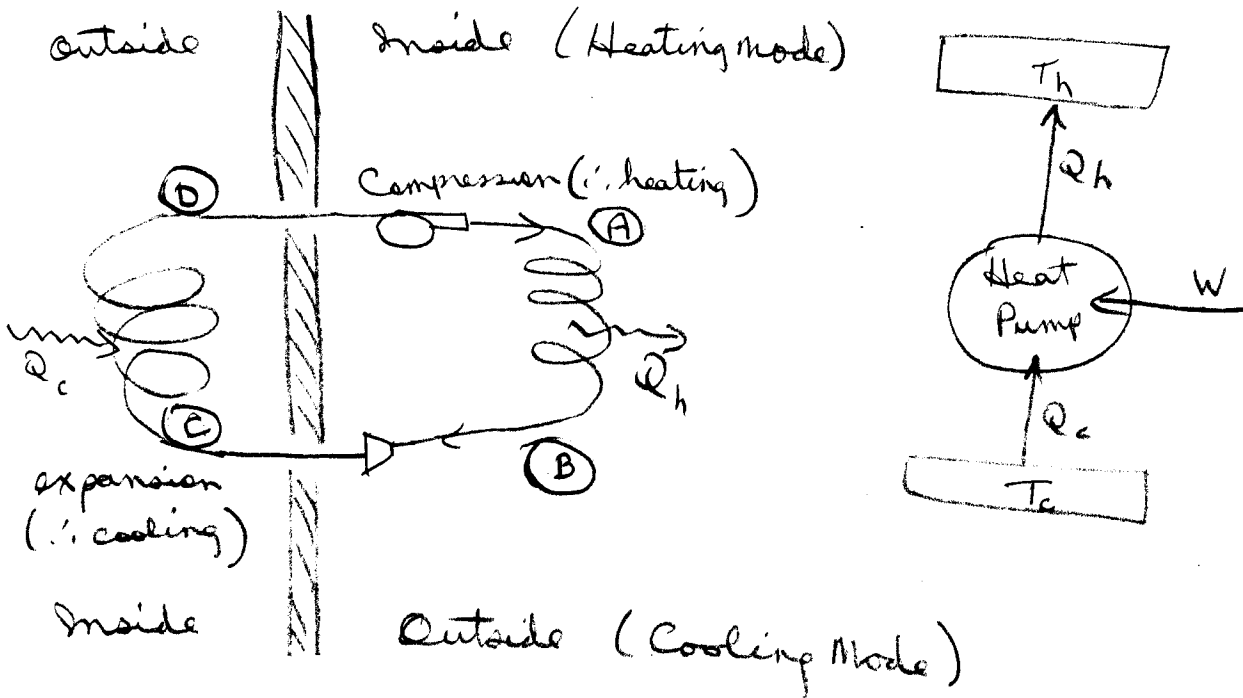
$$\therefore \frac{T_A}{T_B} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_D}{T_C}$$

$$\therefore e = 1 - \frac{T_A}{T_B} = 1 - \frac{T_D}{T_C}$$

Compare to a Carnot cycle:

$$e_{\text{Carnot}} = 1 - \frac{T_{\text{lowest}}}{T_{\text{highest}}} = 1 - \frac{T_A}{T_C} > e_{\text{Otto}}$$

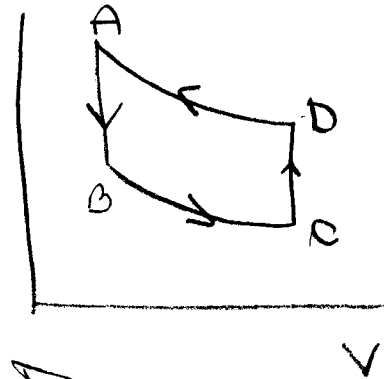
22.6 Heat Pumps and Refrigerators



Carnot cycle in reverse

Coefficient of performance for heat pump

$$\equiv \text{COP} \equiv \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}$$



$\text{COP}_{\text{carnot}} = \text{COP}_{\text{maximum}}$

$$= \frac{T_h}{T_h - T_c}$$

typically ~ 4 when $T_c \sim 25^\circ\text{C}$.

$\text{COP}_{\text{for refrigerator}} \equiv \frac{Q_c}{W}$ (typically ~ 5 or 6)

$$\therefore \text{COP}_{\text{max (refrigerator)}} = \frac{T_c}{T_h - T_c}$$