

Thermodynamics – Lecture 4 Recap

- Finished considering the meaning of reversibility and quasi-static when applied to thermodynamics and see one derivation of the adiabatic equation of state.
- Were introduced to the concept of heat engines.
- Looked at the two statements of the Second Law of Thermodynamics.

$$pV^\gamma = k$$

Thermodynamics – Lecture 5 Aims

- To see the various statements of the Second Law of Thermodynamics and how they are logically equivalent.
- To see the Carnot principles and what they mean for engine efficiency;
- To look at real engine cycles, including the Otto (Petrol) and Diesel cycles, and refrigeration cycles.

First law (energy conservation), even if satisfied some processes don't happen in nature. Second law places a direction on a process. (Arrow of time)

Kelvin Planck – Engine (Tax on converting heat to work)
Clausius – Refrigerator (Nature asymmetric)

Heat pump has $COP_H = 2.5$ to keep house at 20°C . When -2°C outside, the house loses $80,000\text{ kJ/h}$.

$$W_{in} = \frac{|\dot{Q}_H|}{COP_H} = \frac{80,000}{2.5} = 32,000\text{ kJ/h} \quad (8.9\text{ kW}).$$

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 80,000 - 32,000 = 48,000\text{ kJ/hour}.$$

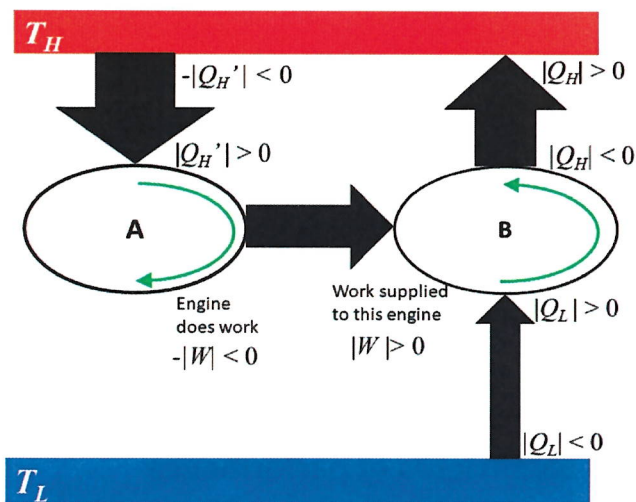


Figure 1: If the Kelvin statement of the Second Law is violated, so is the Clausius.

Engines A and B have the same 'hot' source
A has no heat sink
Work output from A to drive fridge B (engine in reverse)
Fridge takes heat from cold to hot.

More heat returned to hot than originally removed by A. $|Q_H| > |Q_H'|$

Overall: heat transferred from cold to hot, violating Clausius
 $dU = 0$ (cycle) 1st law $dU = \delta Q + \delta W \Rightarrow \delta Q = -\delta W$

Engine A $|Q_H'| = -W$ [Work < 0, engine done by]

Engine B $|W| + |Q_L| = -Q_H$ [Heat rejected is -ve]

Work + heat in from cold Heat rejected

Works are same

$$|Q_H'| + |Q_L| = -Q_H = |Q_H|$$

$$|Q_H'| < |Q_H|$$

More heat back to hot.

Exercise - show a Clausius violator, violates the Kelvin Planck

Carnot Cycles - Two isotherms (high + low temperature) joined by adiabatics.

Carnot realised (2nd Law) that the engine passed through series of equilibrium states, so could be reversed, Reversible engines are as efficient as possible

Showed $\frac{|Q_c|}{Q_H} = \frac{T_c}{T_H}$

Heat ratio equivalent to energy ratio

$\eta = 1 - \frac{|Q_c|}{Q_H}$
General engine

$\eta_{\text{Carnot}} = 1 - \frac{T_c}{T_H}$

Basis of thermodynamic temperature, T is in Kelvin

Carnot Theorem,

- 1) Of all heat engines operating between two temperatures, none is more efficient than a Carnot cycle
- 2) All reversible engines operating between two heat reservoirs have the same efficiency.

Thermodynamics – Handout 5

Proof 10.1: Show that the Carnot relation of heats and temperatures holds

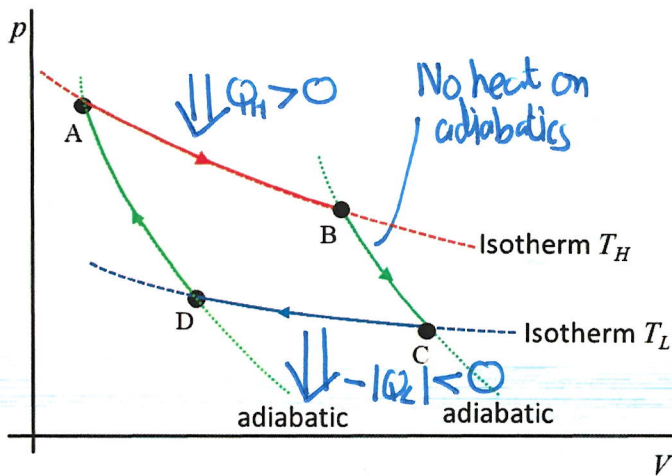


Figure 9: pV diagram of Carnot cycle

$$Q_H = - \int_A^B -pdV = \int_{V_A}^{V_B} \frac{RT_H}{V} dV = RT_H \ln \left(\frac{V_B}{V_A} \right) ; \quad Q_L = RT_L \ln \left(\frac{V_D}{V_C} \right) = -RT_L \ln \left(\frac{V_C}{V_D} \right).$$

$pV = RT_H$ on isotherm

$V_B > V_A \Rightarrow Q_H > 0$

$V_C > V_D, Q_L < 0$

$$\frac{Q_H}{|Q_L|} = \frac{T_H \ln(V_B/V_A)}{T_L \ln(V_C/V_D)}$$

Adiabatic $pV^\gamma = k$
On isotherm

$p_A V_A^\gamma = p_D V_D^\gamma ; \quad p_B V_B^\gamma = p_C V_C^\gamma$ [Two constants]

$p_A V_A = RT_H = p_B V_B ; \quad p_C V_C = RT_L = p_D V_D$

$RT_H V_A^{\gamma-1} = RT_L V_D^{\gamma-1} ; \quad RT_H V_B^{\gamma-1} = RT_L V_C^{\gamma-1}$

$$\frac{T_H}{T_L} = \left(\frac{V_C}{V_B} \right)^{\gamma-1} = \left(\frac{V_D}{V_A} \right)^{\gamma-1} \Rightarrow \left(\frac{V_B}{V_A} \right) = \left(\frac{V_C}{V_D} \right)$$

Volume ratios are same
Sub into heat ratio

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L} \Rightarrow \boxed{\eta = 1 - \frac{T_L}{T_H}}$$

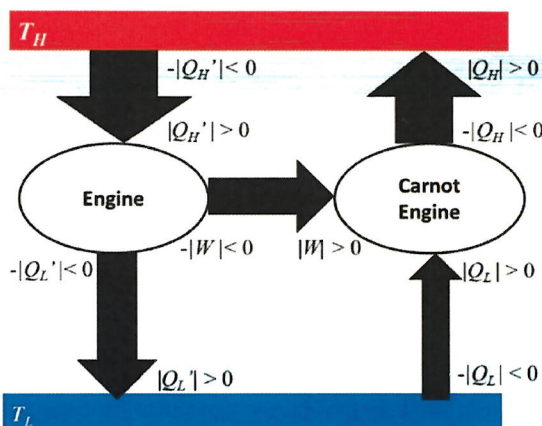


Figure 11: Carnot's First Theorem.

Assume $\eta_{\text{engine}} > \eta_{\text{Carnot}}$

$$|W|/|Q_H'| > |W|/|Q_H|$$

Tells us $|Q_H| > |Q_H'|$

More heat back to hot if engine is more efficient than a Carnot

Violates Clausius Statement

Exercise: Show Carnot's Second Theorem.

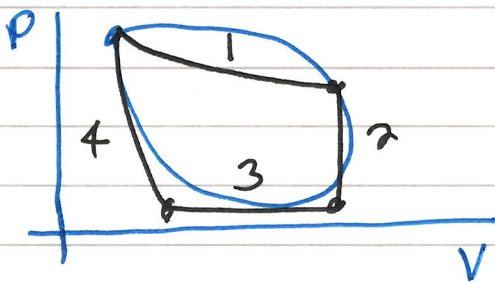
11. Real Engines

Any reversible cycle can run backwards as a fridge. If 'totally reversible' has the same efficiency as a Carnot cycle. In such engines heat is added (from an external source) at constant temperature.

In most engines heat is added across a temperature difference (isochoric/isobaric heating). - these engines are only 'internally reversible' with lower efficiency.

Ideal Carnot cycle, the net work is difference between the two isotherm works; in real engines very difficult to construct the adiabatic processes that join the isotherms. Simplest real engine uses a vapour for the working fluid (easier to compress).

Real engine, not modelled using a Carnot cycle, but we construct it from standard thermo processes in approximations we keep complexities manageable. Remove internal irreversibility (within cycle it is reversible)



Actual

- Model :
- 1) Isotherm
 - 2) Isochoric
 - 3) Isobaric
 - 4) Adiabatic

Otto Cycle - Ideal model of a petrol engine, uses heating at constant volume.

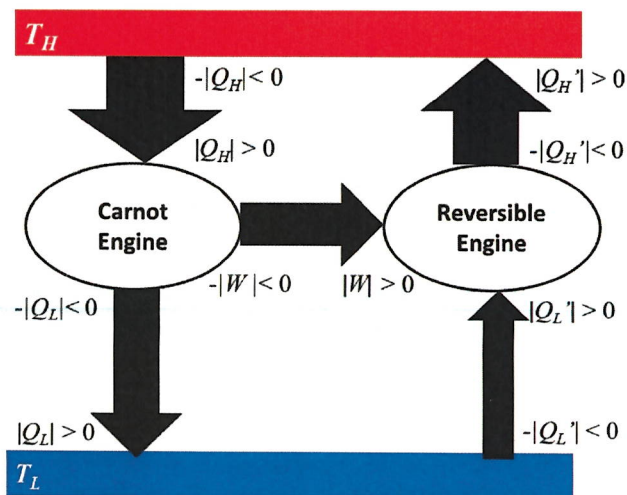


Figure 12: Carnot's Second Theorem.

Proof 11.1: Otto Cycle Efficiency

Cyclic so $dU = 0$ and first law ($dU = \delta Q + \delta W$)

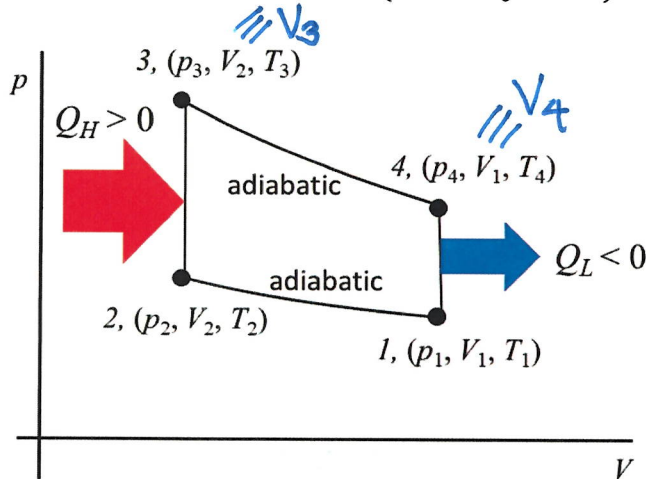


Figure 14: pV diagram of Otto cycle

1→2, Adiabatic compression:

$$Q_{12} = 0 \quad p_1 V_1^\gamma = p_2 V_2^\gamma$$

$$p_1 V_1 = RT_1 \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad (\text{Ⓢ})$$

2→3, Isochoric heating

Absorb heat from series of reservoirs between T_2 and T_3 , dT apart:

$$Q_H = \int_{T_2}^{T_3} C_V dT = C_V (T_3 - T_2) > 0.$$

$$3 \rightarrow 4, \text{ Adiabatic expansion: } p_3 V_3^\gamma = p_4 V_4^\gamma \Rightarrow T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1} \Rightarrow T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

$$4 \rightarrow 1, \text{ Isochoric cooling, heat } Q_L \text{ rejected between } T_4 \text{ and } T_1, Q_L = \int_{T_4}^{T_1} C_V dT = C_V (T_1 - T_4) < 0.$$

$$\eta = 1 - \frac{|Q_L|}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Considering the adiabatic parts, we can write $\frac{T_3 V_2^{\gamma-1}}{T_4} = V_1^{\gamma-1} \Rightarrow \frac{T_1}{T_4} = \frac{T_2}{T_3}$.

Compression Ⓢ $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$

$$\eta = 1 - \frac{T_1 \left(\left(\frac{T_4}{T_1} \right) - 1 \right)}{T_2 \left(\left(\frac{T_3}{T_2} \right) - 1 \right)} \quad \text{Equivalent}$$

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1} = 1 - \left(\frac{V_1}{V_2} \right)^{1-\gamma} = 1 - r^{1-\gamma}.$$

$$r = V_1/V_2 \quad [\text{Amount of compression}]$$