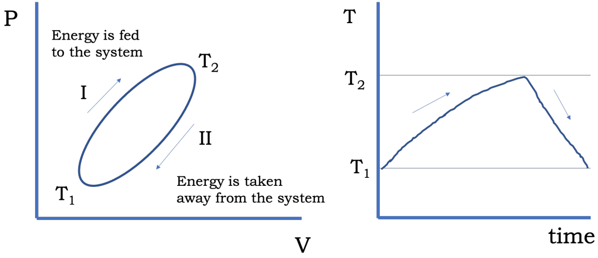
- The first law dealt with the energy conservation and how thermal energy is converted to mechanical energy.
- The second law gives the maximum fraction of the thermal energy that can be really transferred into mechanical energy.

Second Law of thermodynamics

Based on experimental experience: Heat flows by its own only from the warmer body to the colder one, never into the opposite direction.

A quantitative formulation requires understanding of transformation of heat into mechanical work. Hence requires understanding of **thermodynamic cyclic process**.

- Thermodynamic Cycle: A series of processes where a thermodynamic system passes through different states and comes back to the initial state (same thermodynamical variables as initial state).
- Reversible Process



Most periodically operating machines (steam engines or Car motors) - **irreversible cyclic process**. Loose energy during the cycle(Ex: due to friction) which has to be replaced.

- The most famous reversible cyclic process is the **Carnot Cycle**.
- Idealised loss free cycle
- 1824 - Nicolas Sadi Carnot
- Will illustrate the difference between reversible and irreversible processes
- Will enable us to calculate the maximum fraction of heat that can be transformed into mechanical energy. Lead to a quantitative formulation of second law of thermodynamics.

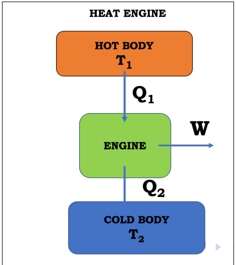
- A reversible cyclic process is one where the cycled system returns to its initial (equilibrium) state on the completion of each cycle with all processes quasi-static and reversible.
- During the cycle the values of the state variables change, with the system exchanging heat as well as mechanical energy with its surroundings.
- The simplest reversible cycle is the Carnot cycle comprising sequentially isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression.
- This is particularly simple because heat is only exchanged along the two isotherms.
- The net work done is represented by the area inside the closed P-V curve.
- The Carnot cycle is useful for illustrating general principles and describing heat engines, heat pumps and refrigerators.
- We will analyse a single cycle, but note that engine power depends on the number of cycles/sec. Isothermal processes tend to be slow, so the Carnot cycle is not useful for practical engines.

Carnot Cycle - 1a

- Assumptions: Any fluid known as the working substance may be taken around the cycle. Obeys Ideal Gas Equation of State: PV = RT (1 mole of ideal gas).
- The surroundings consist of two constant temperature heat reservoirs, one at T_1 and the other at $T_2 < T_1$, and some means (such as pistons) to allow the exchange of mechanical energy with other devices.
- The system and surroundings comprise the hypothetical Carnot engine.
- It operates reversibly between the two heat reservoirs, with, in each cycle, heat Q_1 entering at T_1, Q_2 leaving at T_2 and work W being delivered.

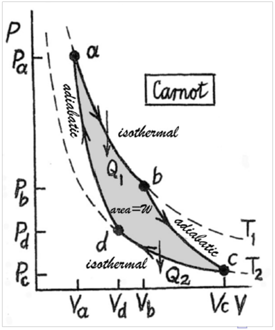
Carnot Cycle - 1b

- Thermodynamic efficiency analysis is done in work/heat per cycle: in reality the power produced is often more important: Power = Work per cycle $\times$ cycles per second
- Q_1, Q_2 and W are heat supplied to, heat rejected by and work done by the working substance.
- The work done on the working substance is -W, and the First Law takes the form $\Delta U = Q_1 - Q_2 + (-W) = 0$ for each complete cycle.
- From this, $W = Q_1 - Q_2$, and the efficiency η of the engine is defined by $\eta = W/Q_1 = 1 - \frac{Q_2}{Q_1}$



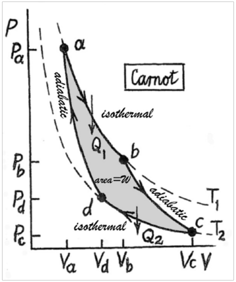
Carnot Cycle - 2

- The four-stage Carnot cycle is shown: Isothermal expansion (a $\rightarrow$ b), Adibatic expansion (b $\rightarrow$ c), Isothermal Compression (c $\rightarrow$ d) and Adiabatic Compression (d $\rightarrow$ a) as it reaches back to its initial state.
- It operates reversibly between the two heat reservoirs, with, in each cycle, heat Q_1 entering at T_1, Q_2 leaving at T_2 and work W being delivered.
- Stages (a): (V_a, P_a, T_1); (b): (V_b, P_b, T_1); (c): (V_c, P_c, T_2); and (d): (V_d, P_d, T_2)



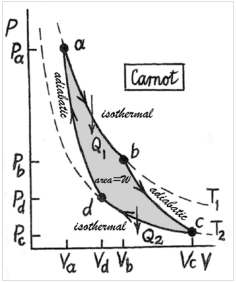
Isothermal Expansion

- a): (V_a, P_a, T_1) to (b): (V_b, P_b, T_1)



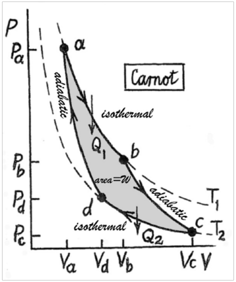
- As per first law dQ = pdV (heat supplied to the system is equal to the mechanical work the system performs during the expansion
- $Q_1 = - W_{ab} = \int_{V_a}^{V_b} PdV = \text{R } T_1 \ln (V_b/V_a)$

- b): $(V_b,\ P_b,\ T_1)$ to (b): $(V_c,\ P_c,\ T_2)$



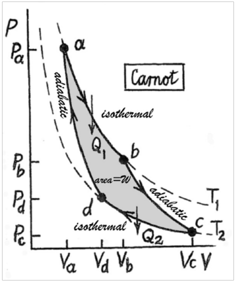
- As per first law dQ = 0 $\Longrightarrow$ dU = -PdV = W_{bc} (Work is performed by the system and delivered to the surrounding, hence negative)
- Decrease in internal energy ΔU = U(T_2) - U(T_1), because $T_2 < T_1$.

- c): $(V_c,\ P_c,\ T_2)$ to (b): $(V_d,\ P_d,\ T_2)$



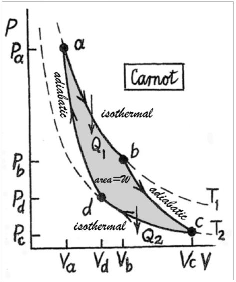
- As per first law dQ = pdV (heat supplied to the system is equal to the mechanical work the system performs during the compression
- $Q_1 = W_{cd} = \int_{V_c}^{V_d} PdV = \mathrm{R}\ T_2 \ln\left(V_c/V_d\right)$
- -$Q_2 > 0$. The heat Q_2 delivered at lower temperature T_2 to the heat reservoir equal to work W_{cd} needed to compress the volume V.

- d): (V_d, P_d, T_2) to (b): (V_a, P_a, T_1)



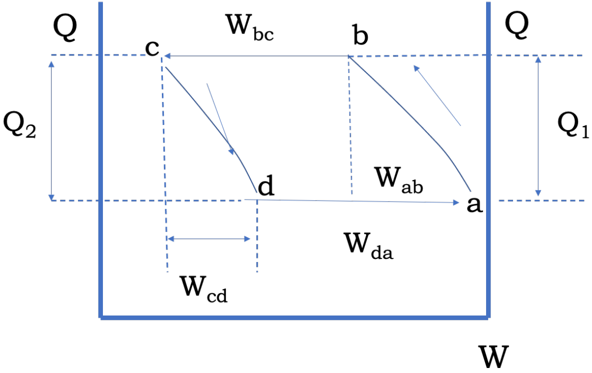
- As per first law dQ $=0$. No heat exchanged. Work is performed during the compression is converted to increase in internal energy
- Increase in internal energy $\Delta U =$ U(T_1) - U(T_2), because $T_2 < T_1$.

- Energy balance : Work delivered to the surrounding in the 2nd process = Work supplied to the system in the 4th process.



- Energy balance : Work delivered in the 2nd process = Work supplied in the 4th process.
- Net energy: Transfer only during isothermal process.
- Net Mechanical Work: $W = W_{ab} + W_{cd} = \mathrm{R}\ T_1 \ln\,(V_a/V_b) + \mathrm{R}\ T_2 \ln\,(V_c/V_d)$

- For Adiabatic process (b) $\Longrightarrow$ (c): $T_1 V_b^{\kappa-1} = T_2 V_c^{\kappa-1}$
- For Adiabatic process (d) $\Longrightarrow$ (a): $T_1 V_a^{\kappa-1} = T_2 V_d^{\kappa-1}$
- Dividing: $\frac{V_b}{V_a} = \frac{V_c}{V_d}$; Ln $\frac{V_c}{V_d}$ = -Ln $\frac{V_a}{V_b}$
- Net Mechanical Work: $W =$ R $(T_1$ - $T_2)$ ln (V_a/V_b).
- The Carnot engine has received the heat Q_1 and has supplied mechanical work $W < 0$ to the outside.
- Such a machine that transfers heat into mechanical energy is called **Heat Engine**.



Net mechanical energy: $W = W_{cd} - W_{ab}$.

- The heat Q_2 supplied to the surrounding is generally lost.
- The efficiency is defined as the ratio of mechanical work supplied by the engine divided by the heat Q_1 put in the engine.
- $\eta = \mid \frac{W}{Q_1} \mid = \frac{R(T_1 - T_2) ln(V_b/V_a)}{R T_1 ln(V_b/V_a)}$
- $\eta = \frac{T_1 - T_2}{T_1}$ – A remarkable result!!
- During the cycle the total received heat cannot be transformed into mechanical work. But only a fraction $\eta < 1 \equiv$ **exenergy**.
- The remaining η-1 (called **Anergy**) is exchanged as heat Q_2 to the surrounding at a lower temperature.
- Conservation of energy: Energy = exenergy + anergy
- η increases as T_1 - T_2 increases $\Longrightarrow$ choose high T_1 and low T_2. But $T_2 \neq 0$ degree Kelvin. Hence, η **is always smaller than unity**.

- When Carnot Cycle is traversed in a opposite direction, heat is transported from the lower temperature T_2 to higher temperature T_1.
- This requires a work: $W = \mathrm{R}\,(T_2 - T_1)\ \ln\,(V_a/V_b)$
- In this case the figure of merit $\equiv$ Co-efficient of performance of a heat pump, $\epsilon_{hp} = \frac{T_1}{T_1 - T_2} = \frac{1}{\eta}$
- The heat pump does not contradict the second law, as heat flow does not occur on its own from colder to hotter place; but needs mechanical work to drive the heat transport.
- There is no periodically working machine with higher efficiency than that of a Carnot Engine. Carnot engine works with an ideal gas and all energy losses are neglected. Real engines have loses that cannot be avoided. Like due to friction of moving pistons, heat conduction to surroundings etc.