## The Clausius statement:

It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

The Kelvin-Planck statement:

It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.
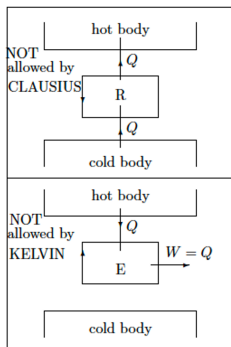
The **R** on the diagram of the forbidden device, denotes **refrigerator**.
The **E** on the diagram of the forbidden device, denotes **engine**.
Note the use of body rather than heat reservoir, meaning that
engines can be considered to operate between two bodies (one a
source and the other a sink of heat) of which the hotter one cools
and the colder one heats up whilst the engine is running.

cold $\xrightarrow{Q}$ hot

is impossible without W

cold $\xleftarrow{Q}$ hot

is possible without W

thermal reservoir

$Q \downarrow$

cyclic engine $\xrightarrow{W}$

first law: $Q = W$, because $\Delta U = 0$ for cycle

second law: This scenario cannot be.

thermal reservoir

$Q \downarrow$

cyclic engine $\xleftarrow{W}$

first law: $Q = W$, because $\Delta U = 0$ for cycle

second law: This scenario can be.

- The equivalence of the Clausius and the Kelvin-Planck statements
- No engine operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.
- All Carnot engines operating between the same two reservoirs have the same efficiency (INDEPENDENT of the working substance).

- $\eta = \frac{W}{Q_1} < 1$ for any heat engine. Heat cannot completely be converted to mechanical work.

- Second Law can be formulated as: (A) Heat flows by its own only from the hot to cold regions, never into the opposite direction. (B) There is no periodically acting machine that can convert heat completely into mechanical work without additional supply of energy. OR: **The realisation of a perpetuum mobile of second kind is impossible**.

- Example of perpetuum mobile of 2nd kind: A ship with engines that receive their energy solely from the heat of the sea. Such a ship could move without additional energy and would not need Oil or Coal.

- New property energy arose via consideration of the first law of thermodynamics
- Entropy: a thermodynamic property that provides a quantitative measure of the disorder of a given thermodynamic state, from consideration of the second law of thermodynamics
- The word itself was coined by Clausius who based it on the combination of $\epsilon\nu$- (en-) "to put into," and $\tau\rho o\pi\eta$ (trope), "turn" or "conversion."
- thermal reservoir at T_{res}, delivers heat $\delta Q'$ to engine, the engine delivers $\delta W'$ work and rejects δQ heat.

- we know from Carnot Cycle discussions $\frac{T_L}{T_H} = \frac{Q_L}{Q_H}$.
- This means $\frac{\delta Q'}{\delta Q} = \frac{T_{res}}{T}$ or $\frac{\delta Q'}{T_{res}} = \frac{\delta Q}{T}$
- From first law we know $\delta W' = \delta Q'$ - dU, which means $\delta W' = T_{res}\frac{\delta Q}{T}$ - dU
- for a thermodynamic cycle $\oint \delta W' = \oint T_{res}\frac{\delta Q}{T}$ - $\oint dU$
- we cannot convert all the heat to work, but we can convert all the work to heat: $W' < 0$. This means $\oint T_{res}\frac{\delta Q}{T} \leq 0$.
- $T_{res} > 0$; $\oint \frac{\delta Q}{T} \leq 0$.
- If all processes are reversible, we lose the inequality, and get simply $\oint \frac{\delta Q}{T} = 0$.

- consider starting from 1, proceeding on path A to 2, and returning to 1 via path B.
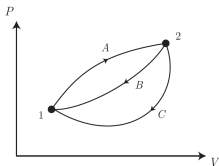
- This means $\int_1^2 \frac{\delta Q_A}{T} + \int_2^1 \frac{\delta Q_B}{T} = 0$.
- same exercise going from 1 to 2 on path A and returning on path C, $\int_1^2 \frac{\delta Q_A}{T} + \int_2^1 \frac{\delta Q_C}{T} = 0$. Subtractung we get $\int_2^1 \frac{\delta Q_B}{T}$ - $\int_2^1 \frac{\delta Q_C}{T} = 0$.
- $\int_2^1 \frac{\delta Q_B}{T} = \int_2^1 \frac{\delta Q_C}{T}$, this imples $\int_1^2 \frac{\delta Q_B}{T} = \int_1^2 \frac{\delta Q_C}{T}$
- Because paths B and C are different and arbitrary, but $\int_1^2 \frac{\delta Q}{T}$ is the same on either path, the integral must be path-independent.
- Defines a thermodynamic property of the system - entropy, S, an extensive quantity S_2 - $S_1 = \int_1^2 \frac{\delta Q}{T}$.

- Introducing this thermodynamic variable, the second law of thermodynamics can be mathematically formulated.
- Reduced Heat: $\frac{dQ}{T}$ - Ration of heat supplied (dQ) to a system at temperature T.
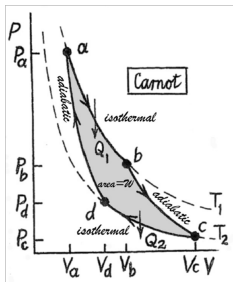
- A system in Carnot cycle can come to (c) in two ways. (a) $\implies$ (b) $\implies$ (c) : Heat exchanged during isothermal process $\frac{Q_1}{T_1}$
- (a) $\implies$ (d) $\implies$ (c) : Heat exchanged during isothermal process $\frac{Q_2}{T_2}$

- For reversible process: $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$.
- Reduced heat (engines) do not depend on the path but only on the initial and final state of the system.

Entropy

Introduce a thermodynamical variable S with dimension $[S] =$ [J]/[K]; $dS = \frac{dQ}{T}$: Change in entropy is the reduced heat exchanged on an infinitesimal part of a reversible process.

- As $\frac{dQ}{T}$ does not depend on the path followed, but solely on the initial and final state of the system, the entropy S, hence like P, T, V, describes a state of the thermodynamic system.

- In a Carnot Cycle; during isothermal process, $\frac{\Delta Q}{T} = \pm$ R ln$\frac{V_2}{V_1}$ = ΔS.
- For a complete reversible process: $\frac{\Delta Q_1}{T_1}$ = - $\frac{\Delta Q_2}{T_2}$ $\Longrightarrow$ For a complete reversible cycle $\Delta S = 0$, implies S is a constant. This process is called **isentropic process**
- Now $\Delta S = 0 \Longrightarrow \Delta Q = 0$ and $T =$ constant. Hence for an isentropic process T has to be kept constant.
- Note for an adiabatic process $\Delta Q = 0$, but T changes.
- From First Law: $dS = \frac{dQ_{rev}}{T} = \frac{dU + PdV}{T}$. Now for one mole of gas, $dU = C_V dT$ and $PV = RT$.
- Hence, $dS = C_V \frac{dT}{T}$ + R $\frac{dV}{V}$
- Integrating and considering **isobaric process**, P = constant: $\Delta S_{isobar} = C_V$ ln $\frac{T_2}{T_1}$ + R ln $\frac{V_2}{V_1}$.
- Similarly considering **isochoric process**, V = constant: $\Delta S_{isochor} = C_P$ ln $\frac{T_2}{T_1}$ + R ln $\frac{P_2}{P_1}$.
- We used: $C_P - C_V$ = R, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
- All these shows S depends on the initial and final state of the system.

■ This considers the heat transfers to a substance as it is taken round an arbitrary cyclic process exchanging heat with any number of surrounding bodies. It can be derived by breaking down the process into equivalent interactions with a large number of Carnot engines and refrigerators.
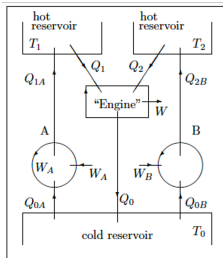
■ 3 different bodies: two Carnot refrigerators A and B and an Engine. The refrigerators are adjusted to exactly the same amount of heat to their hot reservoirs as is taken from those reservoirs by the Engine: ($Q_1 = Q_{1A}$; $Q_2 = Q_{2A}$).

- No such restriction can be put on the heat transfers to and from the cold reservoir and therefore heat owing from it is $Q_{0A} + Q_{0B} - Q_0$.

- The net work done by the composite system is $W - (W_A + W_B)$.

- As no net heat flows into/out of the hot reservoirs. The balance of heat flow and mechanical work (1st Law) for the composite system is $Q_{0A} + Q_{0B} - Q_0 = W - (W_A + W_B)$.

- Since the heat flow is from a single reservoir, the Kelvin-Planck statement of the Second Law would be contradicted if $W > W_A + W_B$. Therefore we must have $W \leq W_A + W_B$ and $Q_{0A} + Q_{0B} - Q_0 \leq 0$.

- From the Carnot refrigerator efficiencies: $Q_{0A} = Q_1 \frac{T_0}{T_1}$ and $Q_{0B} = Q_2 \frac{T_0}{T_2}$.

- the heat entering the cold reservoir: $Q_0 - Q_{0A} - Q_{0B} = Q_0 - (\frac{Q_1}{T_1} + \frac{Q_2}{T_2})T_0 \geq 0 \implies \frac{Q_1}{T_1} + \frac{Q_2}{T_2} - \frac{Q_0}{T_0} \leq 0$.

- Now consider heat inputs q_i to the working substance of the engine. The engine absorbs heat $q_1 = Q_1$ from the hot reservoirs, and returns heat to the cold reservoir, so there is a change of sign: $q_0 = -Q_0$. Hence: $\frac{q_0}{T_0} + \frac{q_1}{T_1} + \frac{q_0}{T_0} \leq 0$.

- If the number of engines and refrigerators is arbitrary, $\sum \frac{q_i}{T_i} \leq 0$. In the limit where the amounts of heat entering the working substance are very small at each step, but the number of steps is very large, $\oint \frac{q}{T} \leq 0$ - **Clausius inequality**

- for reversible cycles : $T_{system} = T_{reservoirs}$ during each heat exchange, $\oint \frac{q}{T} \geq 0$. For both inequalities to be valid simultaneously for reversible cycles only - $\oint \frac{q}{T} = 0$.

- Consider the cycle in the T-S diagram. We start at 1, and proceed to 2 along path I, that represents an irreversible process. We return from 2 to 1 along path R, that represents a reversible process.
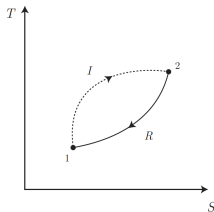
- $0 \geq \oint \frac{\delta Q}{T}$
- The equality implies all processes are reversible; the inequality implies some portion of the process is irreversible. For a reversible process we have $S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$.
- OR $S_1 - S_2 = \int_2^1 \frac{\delta Q}{T}$.
- $0 \geq \int_1^2 \frac{\delta Q_I}{T} + \int_2^1 \frac{\delta Q_R}{T} = \int_1^2 \frac{\delta Q_I}{T} + S_1 - S_2$

- $S_2 - S_1 \geq \int_1^2 \frac{\delta Q_I}{T}$ or in more generally $S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$
- If 1 to 2 is reversible, the equality holds; if 1 to 2 is irreversible, the inequality holds. Now, if the system is isolated, there can be no heat transfer interactions and $\delta Q = 0$, hence $S_2 - S_1 \geq 0$.
- This implies 2 occurs later in time than 1. Thus, for isolated systems, the entropy increases as time moves forward.

- The entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process. This is the principle of increasing entropy.

2nd Law of Thermodynamics

$\Delta S \geq 0$.