

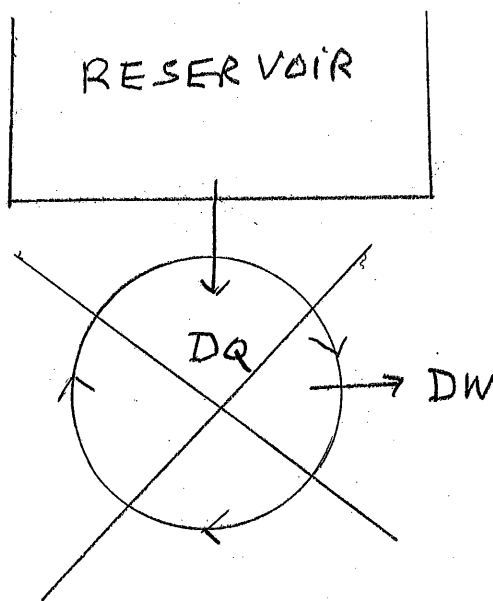
Second Law Of Thermodynamics

MOTIVATION: By now we are fully aware that if two systems are at different temperatures and there is a conducting wall in between they will exchange heat DQ until equilibrium is attained. It is found that in this process the higher temperature reduces and the lower temperature rises $\left[\text{Recall minus sign in the equation } \frac{DQ}{\Delta t} = -kA \frac{\Delta T}{\Delta x} \right]$. The question we need to answer is: why does exchange of heat invariably involve transfer from high T to low T , or, why will heat not "flow" spontaneously from low T to high T ? The Second Law of Thermodynamics was formulated to provide a succinct answer to their question. It will help to define a property which gives DIRECTION to a thermodynamic process.

The starting point comes as follows: we know that 4.18J of mechanical work will mimic the effects of 1 cal of Heat

$$4.18 \text{ J of DW} \Rightarrow 1 \text{ cal of DQ.}$$

and this can be done as often as we like using a cycle. At its simplest level the second law asserts that it is impossible to construct an engine which operates cyclically and whose only effect is to pick up heat DQ from a reservoir and deliver $DW = DQ$. That is, the following schema:

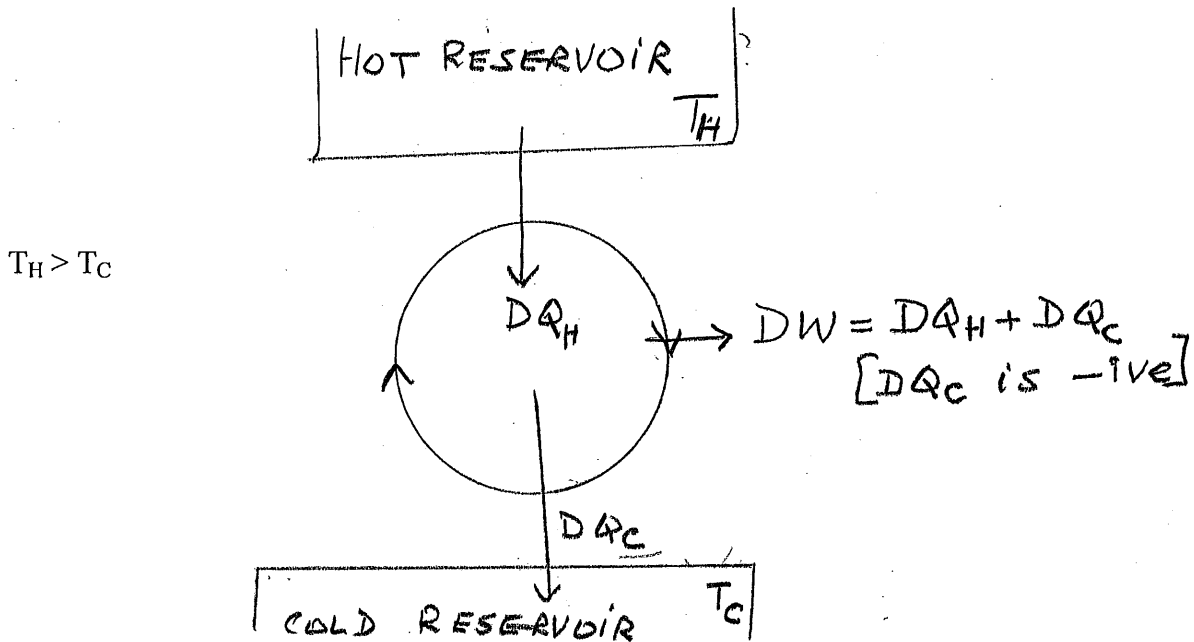


- Is IMPOSSIBLE!!

So already you begin to discern a "Direction" $4.18 \text{ J of DW} \Rightarrow 1 \text{ cal of DQ}$ but the Reverse cannot be done on a repeating basis.

So then, what is possible?

All existing engines produce useful work DW by picking up DQ_H but to do so they must reject DQ_C as shown below:



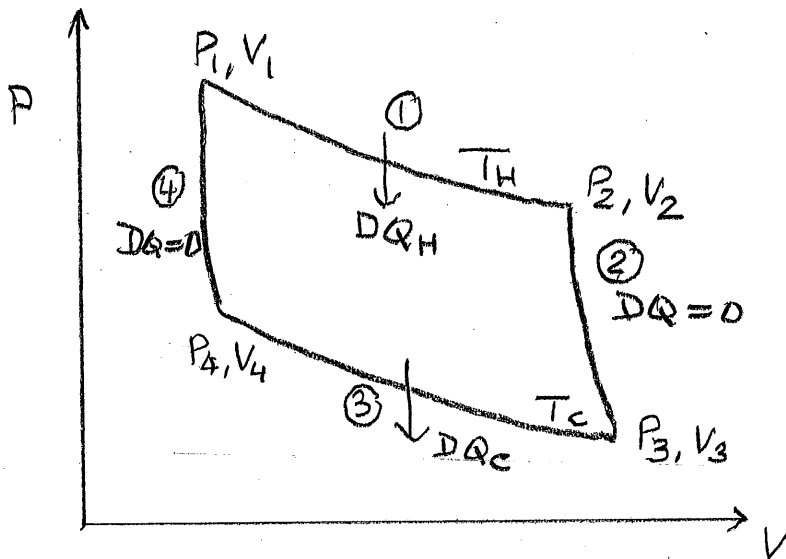
Pick up DQ_H from Hot Reservoir } Produce $(DQ_H + DQ_C)$
 Dump DQ_C into Cold Reservoir } output per cycle

To fulfill the promise that the second law provides a basis for the direction of all thermodynamic processes we must use it to identify a unidirectional property. NOT SURPRISING THAT IT WILL BE CALLED ENTROPY [FROM GREEK WORD $\epsilon\nu\tau\rho\omicron\mu\omicron\psi$].

To do so we discuss a cyclic process proposed by Carnot- Carnot Cycle.

The working substance in our "engine" is going to be an ideal gas so that we can use the equations we wrote for thermodynamic processes.

The cycle is shown in PV- Diagram



We start at P_1, V_1 and carry out 4 processes:

(1) Isothermal Expansion at T_H , we pick up DQ_H from hot reservoir.

$$dU = 0 \quad W = DQ_H = nRT_H \ln \frac{V_2}{V_1} \quad \rightarrow (1)$$

(2) Adiabatic Expansion [$TV^{\gamma-1} = \text{Const}$]. Gas is allowed to cool until temperature is T_C . $DQ = 0$,

$$T_C V_3^{\gamma-1} = T_H V_2^{\gamma-1} \quad \rightarrow (2)$$

(3) Isothermal Contraction at T_C . Discard DQ_C into Cold Reservoir

$$dU = 0 \quad DW = DQ_C = nRT_C \ln \frac{V_4}{V_3} \quad \rightarrow (3)$$

Note: DQ_C is a negative quantity.

Pt. P_4 , V_4 is chosen judiciously so that we can carry out.

(4) Adiabatic Contraction and Gas is allowed to warm up until temperature is back at T_H .

$$T_H V_4^{\gamma-1} = T_C V_3^{\gamma-1} \quad \rightarrow (4)$$

Next, analyze Eqs. (1) through (4)

Combine (1) and (3)

$$\begin{aligned} \frac{DQ_H}{T_H} + \frac{DQ_C}{T_C} &= nR \left[\ln \frac{V_2}{V_1} + \ln \frac{V_4}{V_3} \right] \\ &= nR \left[\ln \frac{V_2 V_4}{V_1 V_3} \right] \\ &= nR \ln 1 \\ &= 0 \end{aligned}$$

Because from (2) and (4)

$$\frac{V_2}{V_3} = \left(\frac{T_C}{T_H} \right)^{\frac{1}{\gamma-1}} = \frac{V_1}{V_4}$$

That is,

$$\boxed{\frac{DQ_H}{T_H} + \frac{DQ_C}{T_C} = 0} \quad \rightarrow (A)$$

This has two very fundamental consequences:

I. Efficiency of our engine.

$$\eta = \frac{\text{Output}}{\text{Input}} = \frac{DQ_H + DQ_C}{DQ_H} = 1 - \frac{T_C}{T_H}$$

$\Rightarrow \eta$ is determined SOLELY by ratio of TEMPERATURES!

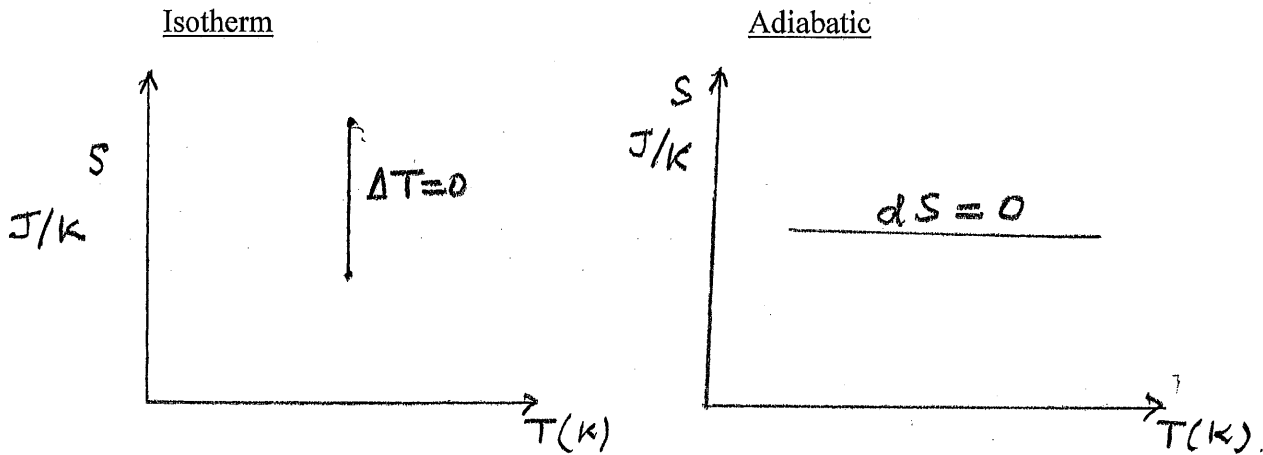
II. If we define a new property by the equation $dS = \frac{DQ}{T}$

The change in S over a closed loop is ZERO!! S is unique. It is appropriate to use d, Change in S independent of Path.

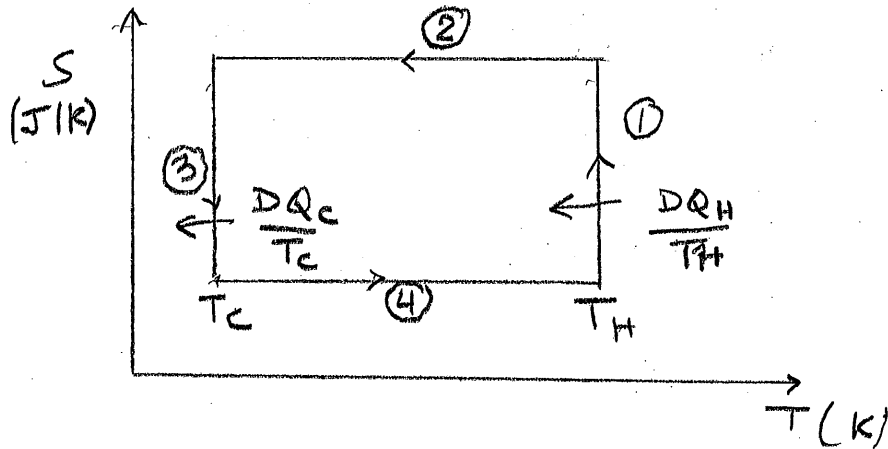
S is called ENTROPY.

defines $dS = \frac{R DQ}{T}$ (B)

change of Entropy in a REVERSIBLE PROCESS.
CARNOT CYCLE IN S-T DIAGRAM.

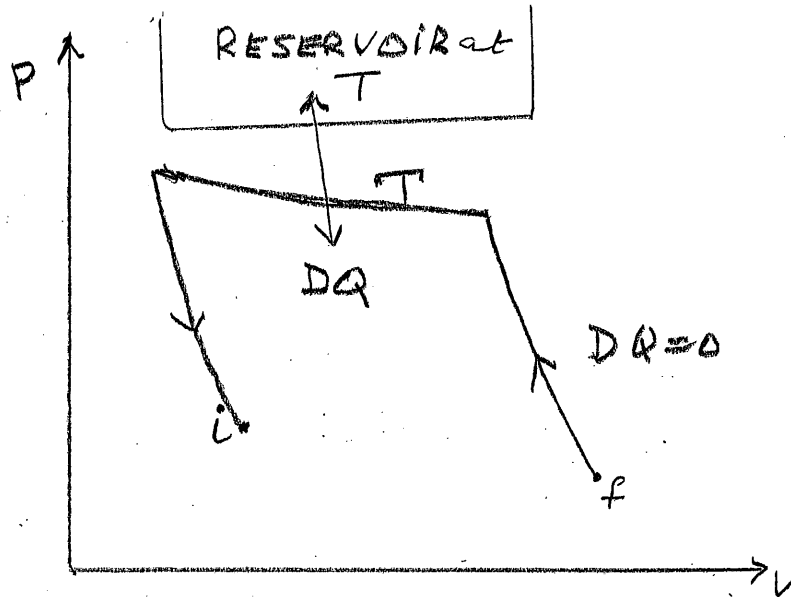


Cycle



Is the Quantity defined in (B) unidirectional? The answer is yes. To prove it we proceed as follows:

Imagine that we carry out an IRREVERSIBLE ADIABATIC PROCESS – $DQ = 0$, but only initial and final state is in equilibrium so only they are represented on the P-V diagram.



Since i and f are equilibrium states, we can assign values S_i and S_f to them. Next, carry out three reversible processes.

$f \rightarrow A$ reversible adiabatic, $DQ = 0$ and by

$$\text{Eq.(B)} \quad dS = 0, \quad \text{so} \quad S_A = S_f$$

$A \rightarrow B$ reversible isotherm where system exchanges DQ with reservoir.

Choose B carefully so that

$B \rightarrow A$ reversible adiabatic [$(DQ) = 0$] takes us back to i . Again, $\Delta S = 0$, so $S_B = S_i$.

Altogether, we have an irreversible cycle $i \rightarrow f \rightarrow A \rightarrow B \rightarrow i$ in which the only heat exchange is with the single reservoir at T . The second law forbids one taking DQ from the reservoir and converting it to DW .

It only allows us to discard DQ into the reservoir.

$$dS_{AB} = \frac{DQ}{T} = S_B - S_A < 0$$

so $S_B < S_A$ and indeed $S_f > S_i$

That is, in an irreversible adiabatic $DQ = 0$, but

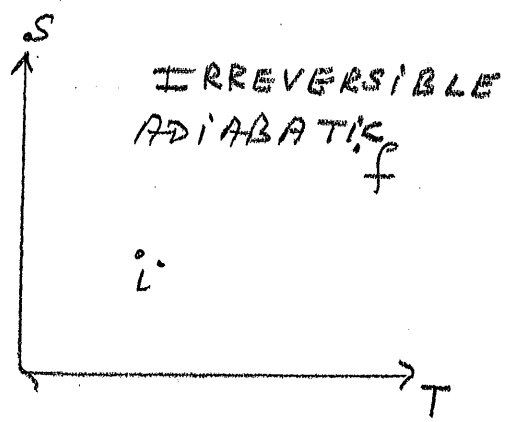
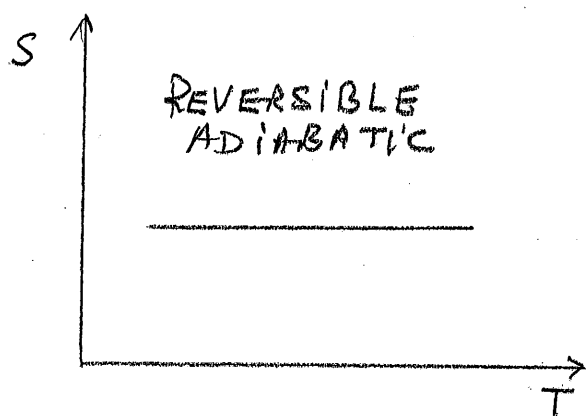
$$dS > 0$$

So indeed change of S is unidirectional. In an adiabatic process S can only increase except in limiting case when process is reversible when $dS = 0$.

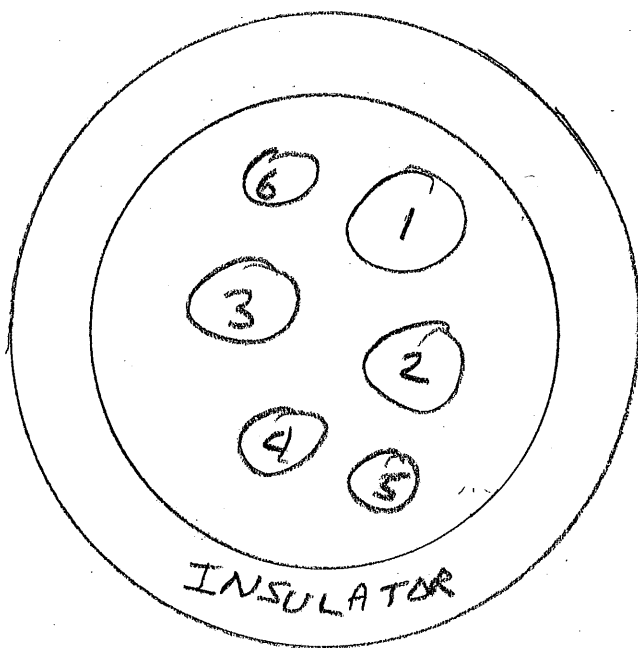
To summarize, in terms of entropy, 2nd law says:

$$dS \geq 0$$

in any adiabatic process.



NOTE: FINAL STEP IN ARGUMENT IS THAT ANY PROCESS CAN BE RENDERED ADIABATIC BY PUTTING THE INSULATING BOUNDARY OUTSIDE ALL OF THE SYSTEMS INVOLVED IN THE PROCESS.



$$dS = \left(\sum dS_i \right) \geq 0$$