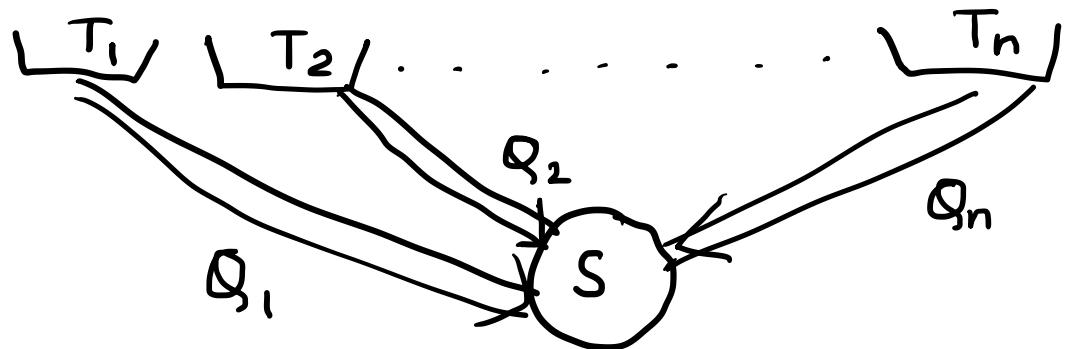


Some properties of cycles

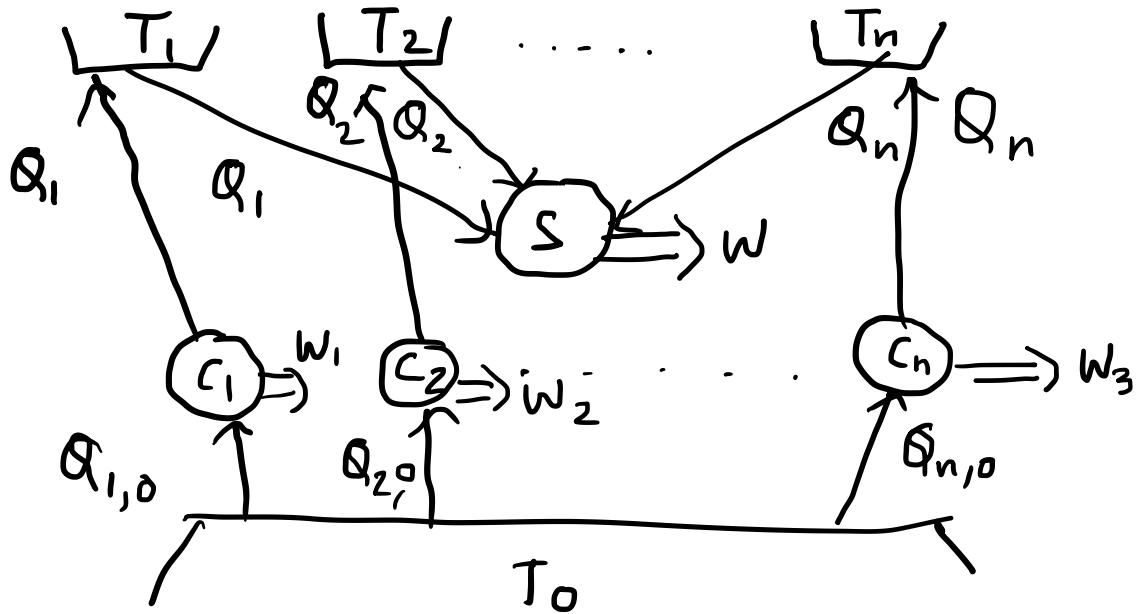
System S operating in a cycle



$Q > 0$ heat absorbed by system
 $Q < 0$ heat rejected

Claim

$$\boxed{\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0}$$



Add a source at T_0
 Add n Carnot cycles
 such that heat
 given up at source T_i
 $= Q_i$

For a Carnot cycle

$$\frac{Q_{i,o}}{Q_i} = \frac{T_0}{T_i}$$

$$Q_{i,o} = \frac{T_0}{T_i} Q_i$$

Composite cycle of S & n Carnot engines.

- Net heat exchanged at $T_1 \dots T_n = 0$
- Source T_0 loses an amt of heat = \sum of heat absorbed by $C_1 \dots C_n$.

Total heat surrendered by source T_0

$$Q_0 = \sum_{i=1}^n Q_{i,0} = T_0 \sum_{i=1}^n \frac{Q_i}{T_i}$$

Net result: "Composite system receives heat Q_0 from source T_0 (without rejecting heat to second source) works it completely to work over a cycle

Violates Kelvin-Planck statement if $Q_0 > 0$

$$\therefore Q_0 \leq 0$$

$$T_0 \sum_{i=1}^n \frac{Q_i}{T_i} \leq 0 \quad T_0 > 0$$

$$\boxed{\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0}$$

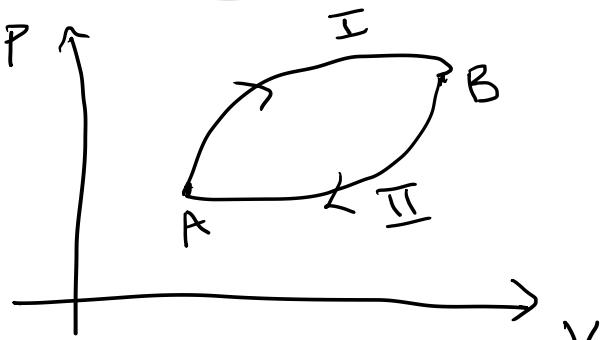
If cycle S is reversible, run backwards

$$\sum_{i=1}^n -\frac{Q_i}{T_i} \leq 0, \quad \left. \begin{aligned} \sum_{i=1}^n \frac{Q_i}{T_i} &\geq 0 \\ \sum_{i=1}^n \frac{Q_i}{T_i} &= 0 \end{aligned} \right\} \Rightarrow \text{reversible}$$

Generalize to continuum of sources

$$\oint \frac{dQ}{T} \leq 0$$

Entropy



Cyclic reversible transformation

$$\oint \frac{dQ}{T} = 0$$

$$\left(\int_A^B \frac{dQ}{T} \right)_I + \left(\int_B^A \frac{dQ}{T} \right)_{II} = 0$$

$$\left(\int_A^B \frac{dQ}{T} \right)_I = \left(\int_A^B \frac{dQ}{T} \right)_{II} \Rightarrow \text{independent of path}$$

This enables us to define a new state fn. (on par with V, T, P, U etc.)
called entropy

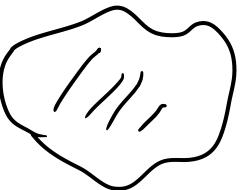
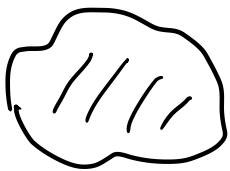
$$S(A) = \int_0^A \frac{dQ}{T} \quad \Rightarrow \text{over a reversible path}$$

Standard State

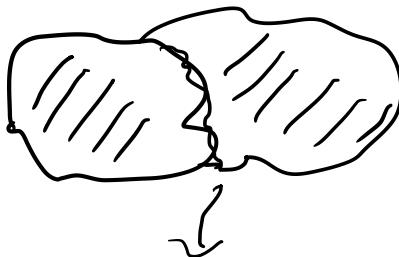
$$S(B) - S(A) = \left(\int_A^B \frac{dQ}{T} \right)$$

Infinitesimal form $dS = \frac{dQ}{T}$

Entropy is often additive, i.e. entropy of system composed of several parts = sum of entropy of parts.



two homogeneous substances



surface energy
can be neglected?

you need

$$U = U_1 + U_2 \dots ?$$

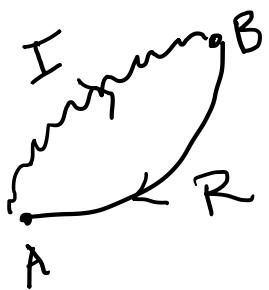
$$W = W_1 + W_2$$

$$Q = Q_1 + Q_2$$

$$\Rightarrow S = S_1 + S_2$$

works where $U = U_1 + U_2$

Further properties of entropy



$$S(B) - S(A) = \left(\int_A^B \frac{dQ}{T} \right)_{\text{rev}} . \quad \checkmark$$

We will show that

$$S(B) - S(A) \geq \int_A^B \frac{dQ}{T}$$

Closed path AIBRA

$$0 \geq \oint_{AIBRA} \frac{dQ}{T} = \left(\int_A^B \frac{dQ}{T} \right)_I + \left(\int_B^A \frac{dQ}{T} \right)_R$$

but $\left(\int_B^A \frac{dQ}{T} \right)_R = S(A) - S(B)$

$$0 \geq \left(\int_A^B \frac{dQ}{T} \right)_I - (S(B) - S(A))$$

$$S(B) - S(A) \geq \int_A^B \frac{dQ}{T}$$

Proved.

For a completely isolated system $\rightarrow dQ = 0$

$$S(B) \geq S(A)$$

For any transformation of an isolated system, the entropy of the final state can NEVER be less than that of the initial state

No process can decrease the entropy

When an isolated system is in a state of maximum entropy consistent with its energy, it cannot undergo any further transfr. because any transfr. would decrease its entropy

State of maximum entropy \Rightarrow stable state.