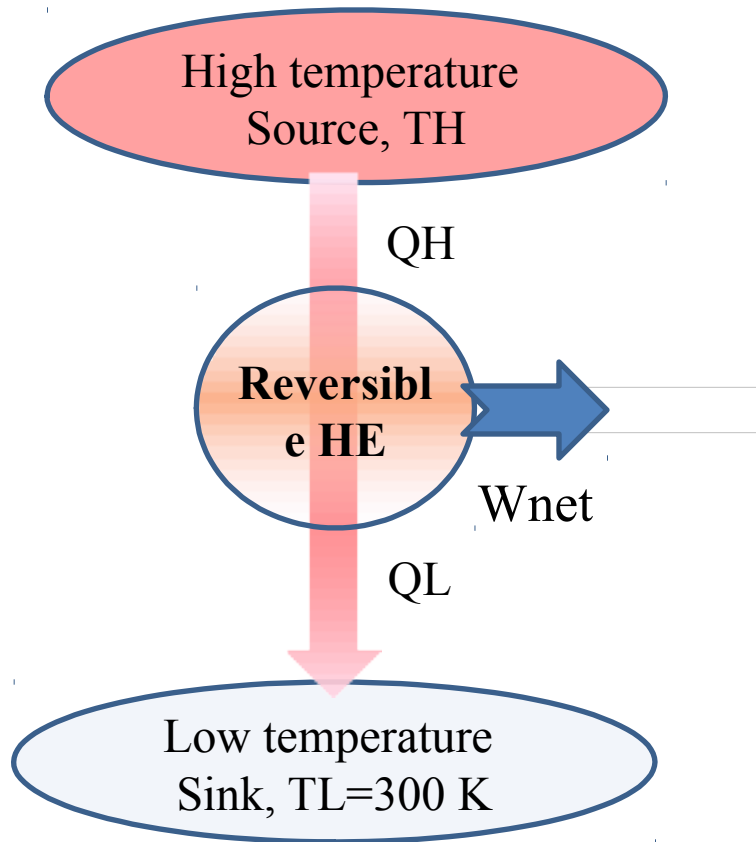


- Recap: Lecture 12: 6th Feb 2014, 0930-1030 hrs.
 - Carnot principles
 - Proof of the Carnot principles
 - Thermodynamic temperature scale

Quality of energy



$T_H, \text{ K}$	$\eta_{th}, \%$
1000	70
700	57.1
500	40
400	25
350	14.3

Quality of energy

- Energy has quality as well as quantity.
- More of the high-temperature thermal energy can be converted to work.
- The higher the temperature, the higher the quality of the energy.
- Work is a high quality form of energy than heat since 100 percent of work can be converted to heat, but only a fraction of heat can be converted to work.

Carnot refrigerator and heat pump

- Operates on a reversed Carnot cycle.
- The coefficients of performance are:

$$\begin{aligned} COP_R &= \frac{1}{Q_H / Q_L - 1} & COP_{HP} &= \frac{1}{1 - Q_L / Q_H} \\ \text{or, } COP_R &= \frac{1}{T_H / T_L - 1} & COP_{HP} &= \frac{1}{1 - T_L / T_H} \end{aligned}$$

- These are the highest coefficients of performance that a refrigerator or a heat pump operating between the temperature limits of T_L and T_H can have.

Carnot refrigerator and heat pump

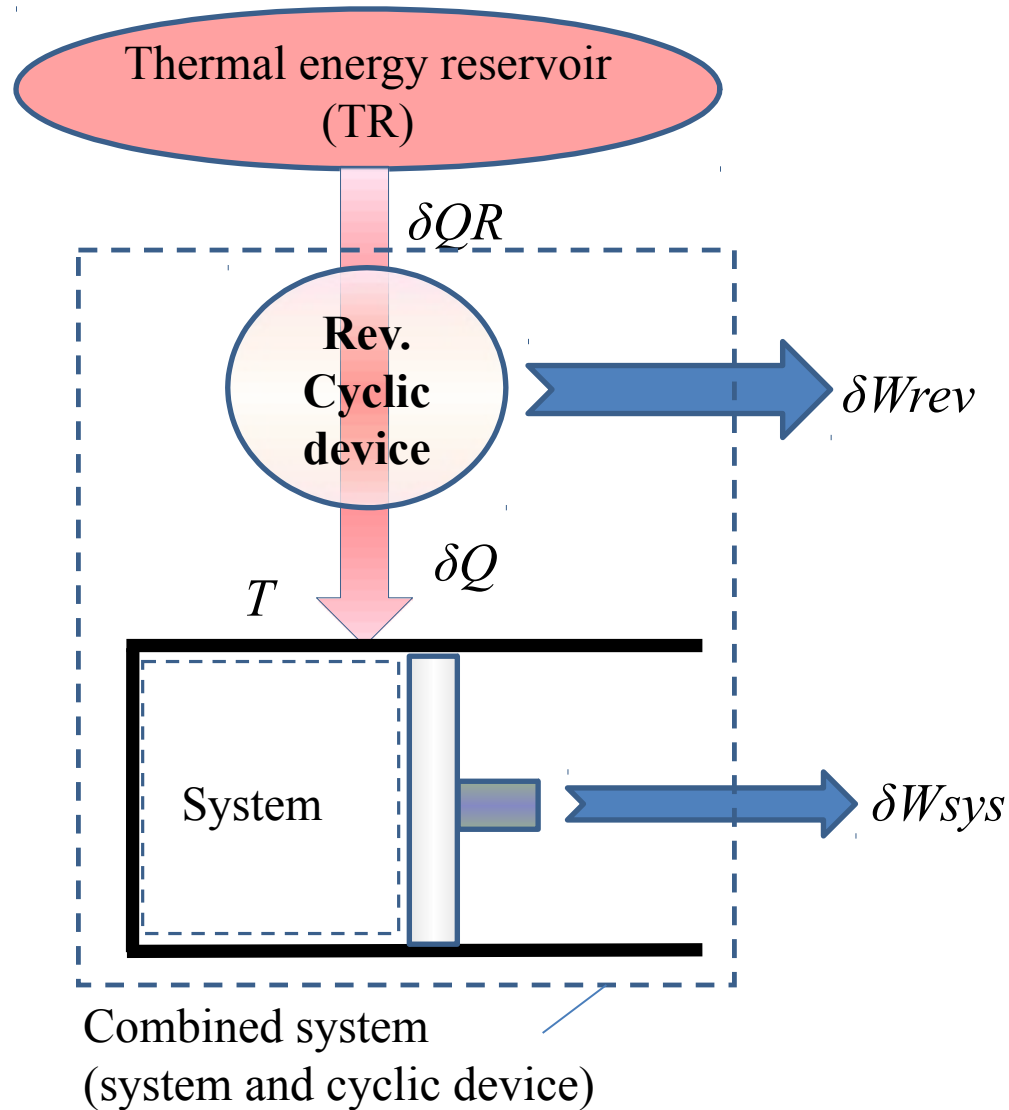
$$COP_{R/HP} \begin{cases} < COP_{R/HP, reversible} & \text{Irreversible} \\ = COP_{R/HP, reversible} & \text{Reversible} \\ > COP_{R/HP, reversible} & \text{Impossible} \end{cases}$$

From thermodynamic temperature scale

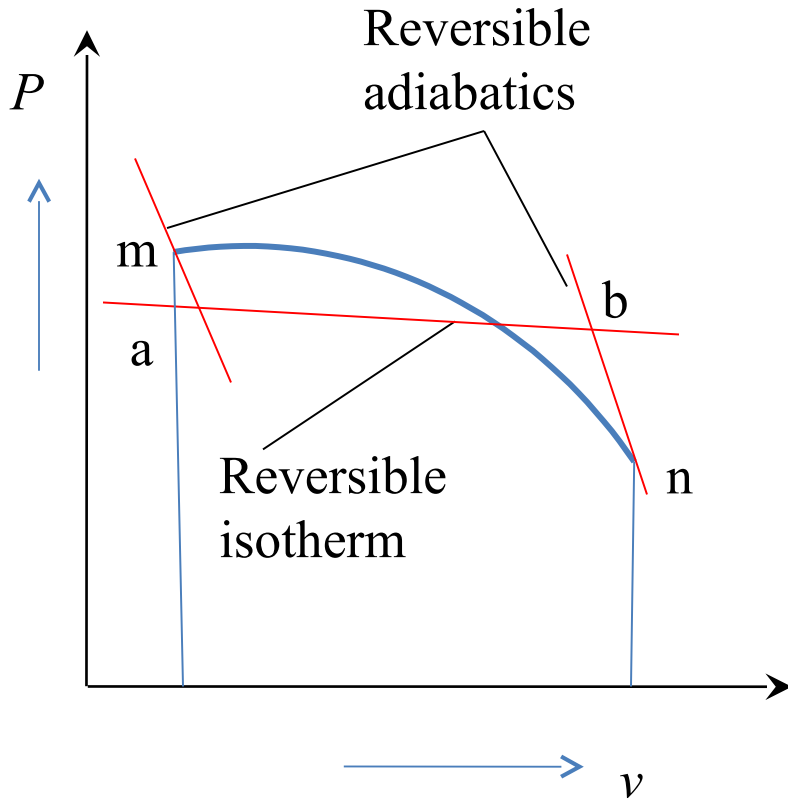
- Lord Kelvin proposed $\phi(T) = T$ to define a thermodynamic scale as

$$\left(\frac{Q_H}{Q_L} \right)_{rev} = \frac{T_H}{T_L}$$
$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Clausius inequality



Reversible adiabatics



Process m-n

$$Q_{m-n} = U_n - U_m + W_{mn}$$

Process m-a-b-n

$$Q_{m-a-b-n} = U_n - U_m + W_{m-a-b-n}$$

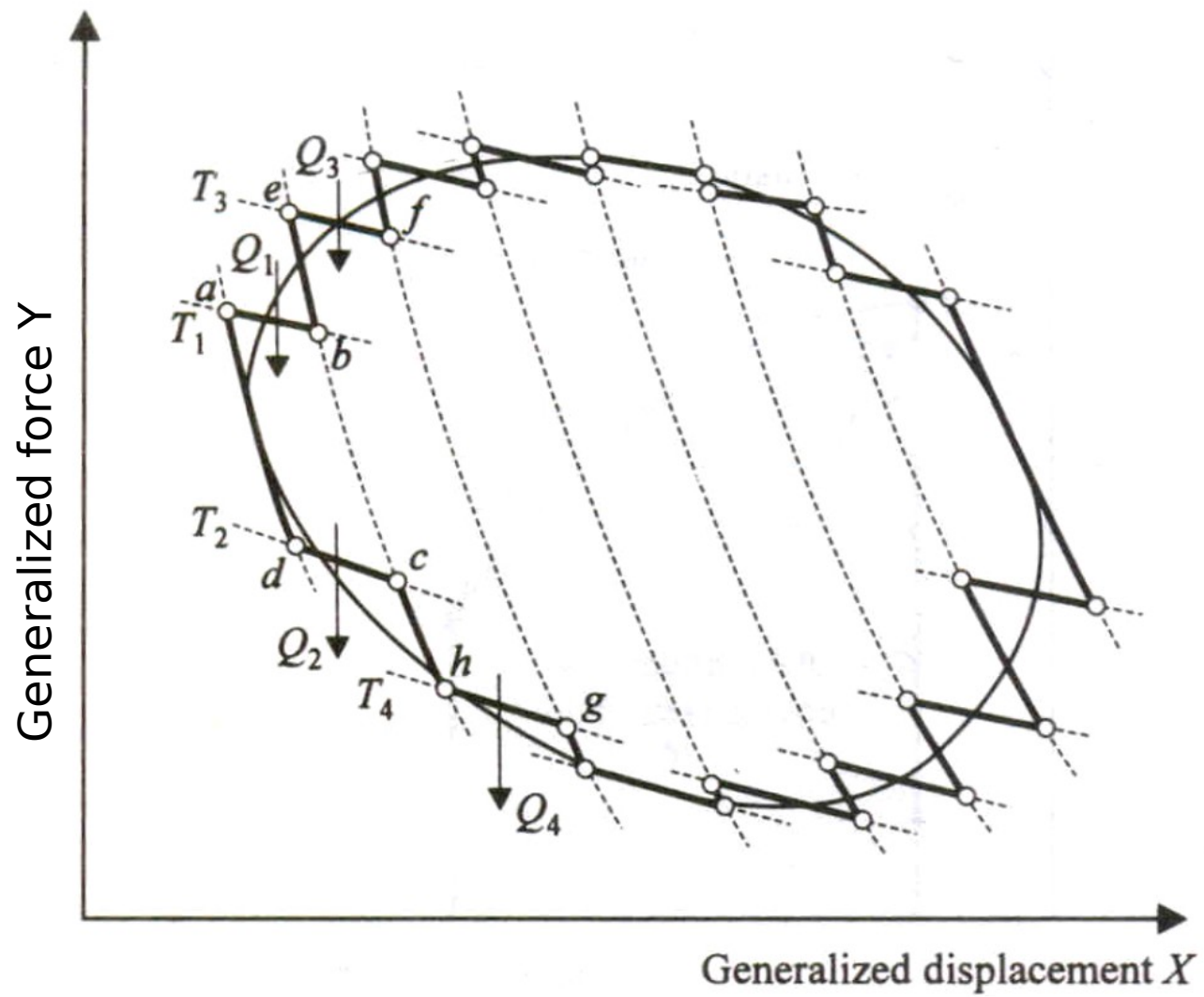
Since, $W_{m-a-b-n} = W_{mn}$

$$\begin{aligned} Q_{m-n} &= Q_{m-a-b-n} \\ &= Q_{m-a} + Q_{a-b} + Q_{b-n} \end{aligned}$$

Since $Q_{m-a} = 0$, $Q_{b-n} = 0$

$$Q_{m-n} = Q_{a-b}$$

Reversible path can be substituted by two reversible adiabatics and a reversible isotherm



$$\frac{|Q_2|}{T_2} = \frac{|Q_1|}{T_1}$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

or

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \dots = 0$$

$$\sum_j \frac{Q_j}{T_j} = 0$$

Clausius inequality

- Applying the energy balance to the combined system identified by dashed lines yields: $\delta WC = \delta QR - dEC$
- where δWC is the total work of the combined system ($\delta W_{rev} + \delta W_{sys}$) and dEC is the change in the total energy of the combined system.
- Considering that the cyclic device is a reversible one

$$\frac{\delta Q_R}{T_R} - \frac{\delta Q}{T}$$

Clausius inequality

- From the above equations:

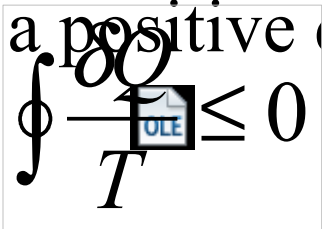
$$\delta W_C = T_R \frac{\delta Q}{T} - dE_C$$

- Let the system undergo a cycle while the cyclic device undergoes an integral number of cycles

$$W_C = T_R \oint \frac{\delta Q}{T}$$

- Since the cyclic integral of energy is zero.

Clausius inequality

- The combined system is exchanging heat with a single thermal energy reservoir while involving (producing or consuming) work WC during a cycle. Hence WC cannot be a work output, and thus it cannot be a positive quantity.
- Considering TR to be a positive quantity,

$$\oint \frac{\delta Q}{T} \leq 0$$
- This is the Clausius inequality.

Clausius inequality

- Clausius inequality is valid for all thermodynamic cycles, reversible or irreversible, including the refrigeration cycles.
- If no irreversibilities occur within the system as well as the reversible cyclic device, then the cycle undergone by the combined system is internally reversible.

$$\oint \left(\frac{\delta Q}{T} \right)_{\text{int.rev}} = 0$$

Clausius inequality

- Clausius inequality provides the criterion for the irreversibility of a process.

$\oint \frac{\delta Q}{T} = 0$, the process is reversible.

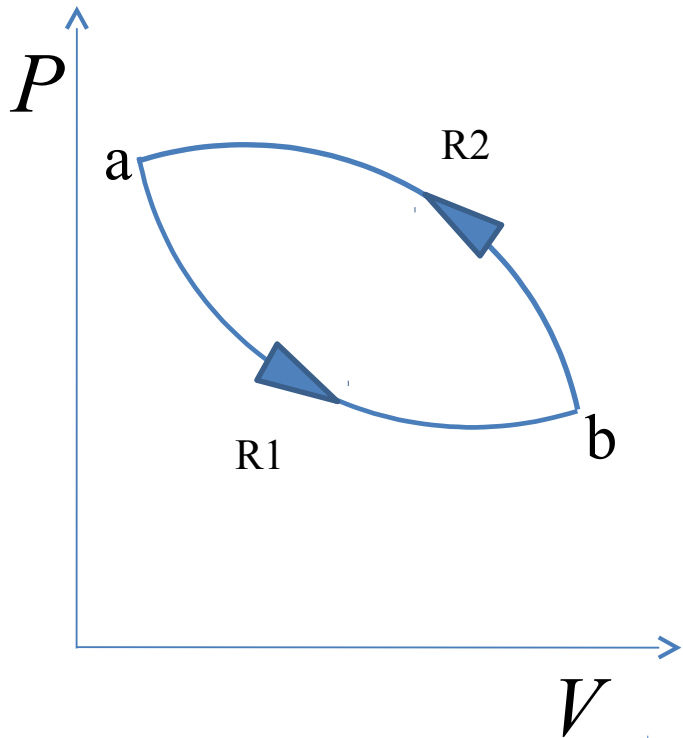
$\oint \frac{\delta Q}{T} < 0$, the process is irreversible and possible.

$\oint \frac{\delta Q}{T} > 0$, the process is impossible.

Clausius inequality and entropy

- The cyclic integral of work and heat are not zero.
- However, the cyclic integral of volume (or any other property) is zero.
- Conversely, a quantity whose cyclic integral is zero depends on the state only and not the process path, and thus it is a property
- Clausius realized in 1865 that he had discovered a new thermodynamic property, and he chose to name this property **entropy**.

The property of entropy



$$\oint_{R_1 R_2} \frac{dQ}{T} = 0$$

$$R1 \int_a^b \frac{\delta Q}{T} + \int_{R2}^a \frac{\delta Q}{T} = 0$$

$$\text{or, } \int_{R1}^b \frac{\delta Q}{T} = - \int_{R2}^a \frac{\delta Q}{T}$$

Since R_2 is a reversible path,

$$R1 \int_a^b \frac{\delta Q}{T} = \int_a^b \frac{\delta Q}{T}$$

The property of entropy

- $\int_a^b \frac{\delta Q_R}{T}$ is independent of the reversible path connecting a and b .
- This property whose value at the final state minus the initial state is equal to $\int_a^b \frac{\delta Q_R}{T}$ is called **entropy**, denoted by S .

$$\int_a^b \frac{\delta Q_R}{T} = S_b - S_a$$

- When the two equilibrium states are infinitesimally near,

$$\frac{\delta Q_R}{T} = dS$$

Entropy

- Entropy is an extensive property of a system and sometimes is referred to as **total entropy**. Entropy per unit mass, designated s , is an intensive property and has the unit kJ/kg·K
- The entropy change of a system during a process can be determined by

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{int. rev.}} \quad (\text{kJ/kg})$$

Entropy

- Entropy is a property, and like all other properties, it has fixed values at fixed states.
- Therefore, the entropy change dS between two specified states is the same no matter what path, reversible or irreversible.

Temperature-entropy plot

$$dS = \frac{\delta Q_{rev}}{T}$$

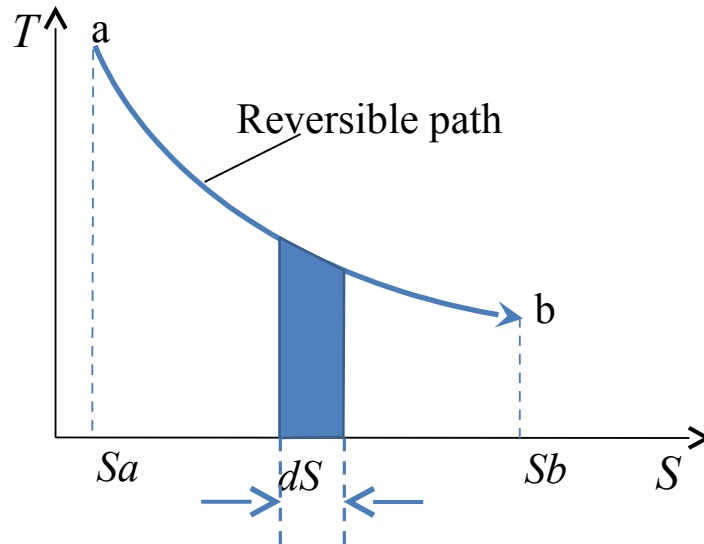
If the process is reversible and adiabatic, $\delta Q_{rev} = 0$
 $\therefore dS = 0$ or $S = \text{constant}$

- A reversible adiabatic process is, therefore, and isentropic process.

$$\delta Q_{rev} = TdS$$

or, $Q_{rev} = \int TdS$

Temperature-entropy plot



$$Q_{rev} = \int_a^b T dS = T(S_b - S_a)$$

- The area under the reversible path on the T-S plot represents heat transfer during that process.

Isentropic processes

- A process where, $\Delta s=0$
- An isentropic process can serve as an appropriate model for actual processes.
- Isentropic processes enable us to define efficiencies for processes to compare the actual performance of these devices to the performance under idealized conditions.
- A reversible adiabatic process is necessarily isentropic, but an isentropic process is not necessarily a reversible adiabatic process.