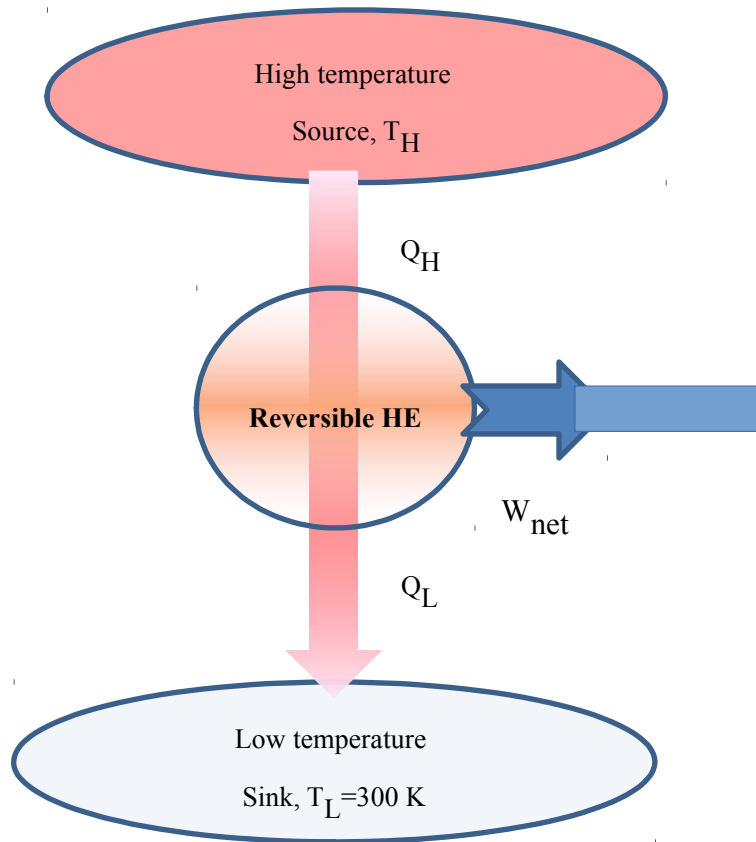- Recap: Lecture 12: 6th Feb 2014, 0930-1030 hrs.
  - Carnot principles
  - Proof of the Carnot principles
  - Thermodynamic temperature scale

Quality of energy

| High temperature Source, T_H |
| Reversible HE |
| Low temperature Sink, $T_L = 300$ K |

Q_H

W_{net}

Q_L

T_H, K	η_{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:

$$COP_R = \frac{1}{Q_H / Q_L - 1} \qquad COP_{HP} = \frac{1}{1 - Q_L / Q_H}$$

$$or, \quad COP_R = \frac{1}{T_H / T_L - 1} \qquad COP_{HP} = \frac{1}{1 - T_L / T_H}$$

- 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.
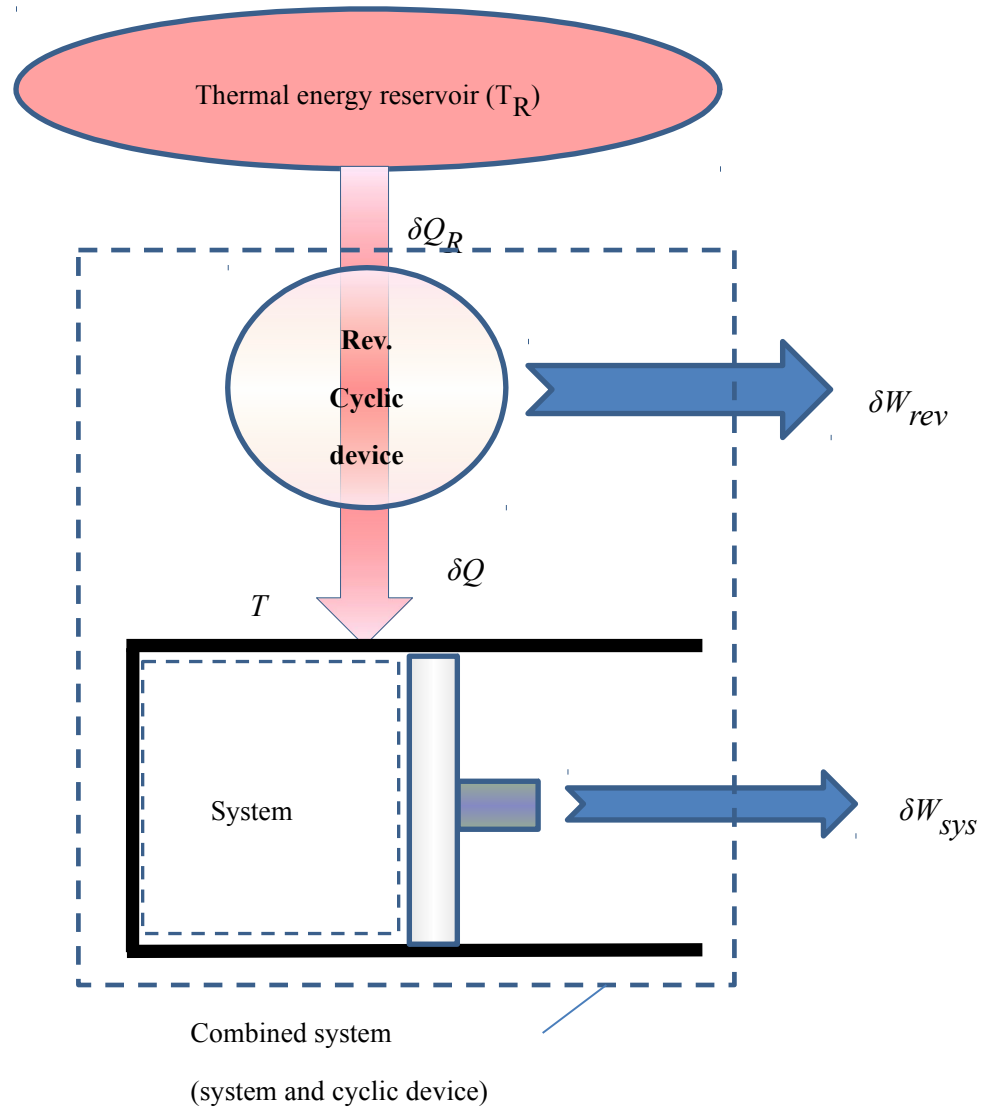
Carnot refrigerator and heat pump

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

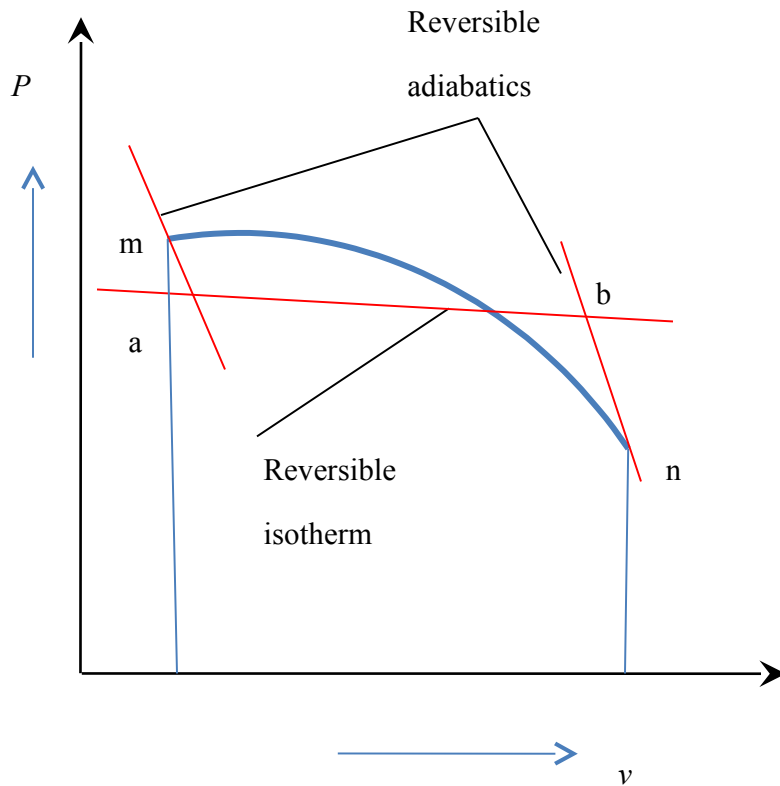# From thermodynamic temperature scale

- Lord Kelvin proposed   to defi $\phi(T) = T$

  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

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

Process m-a-b-n

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

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

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

$$= Q_{m\text{-}a} + Q_{a\text{-}b} + Q_{b\text{-}n}$$

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

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

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

Generalized force Y

Generalized displacement X
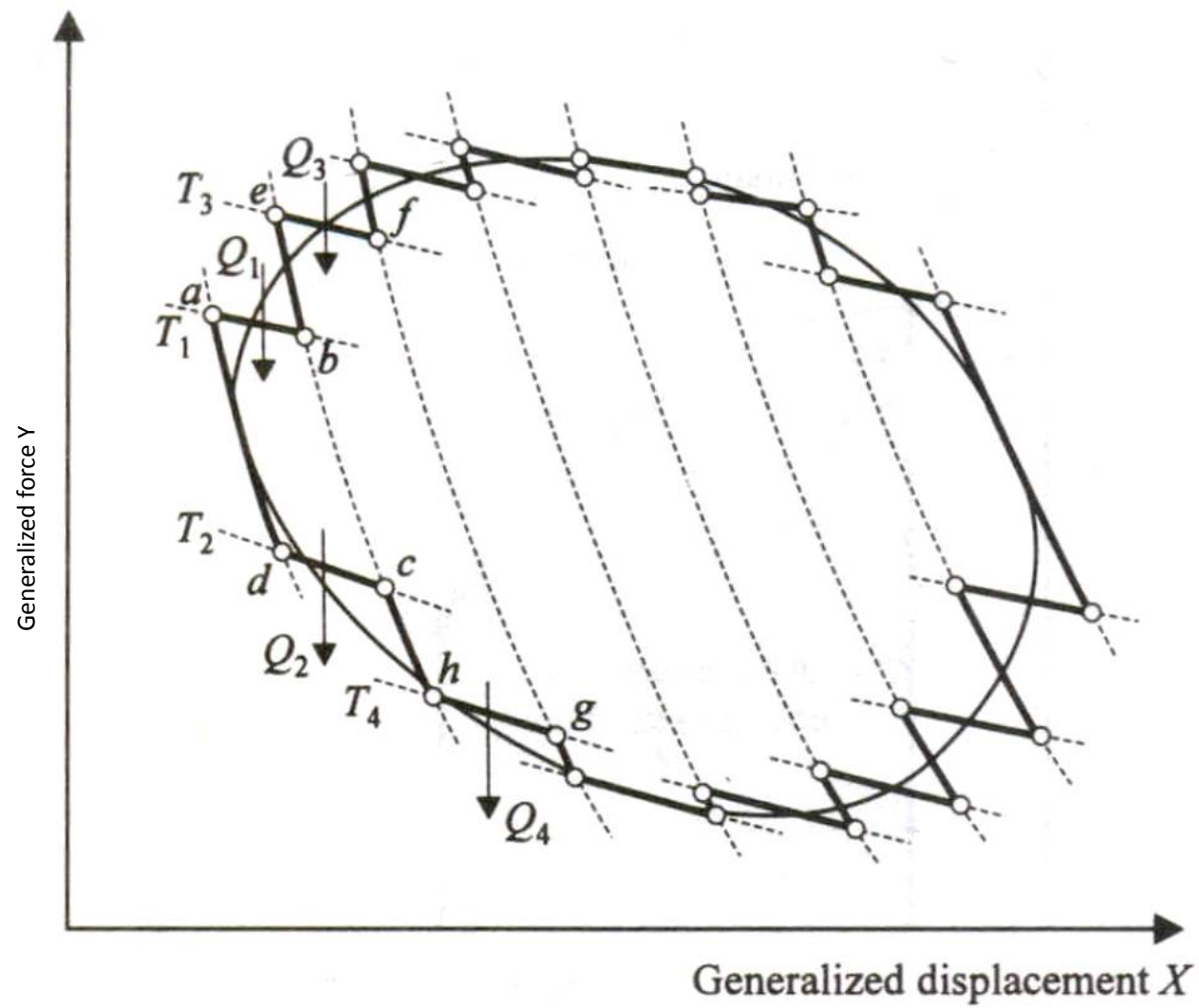
$$\frac{|Q_2|}{T_2} = \frac{|Q_1|}{T_1}$$

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

or

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

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

Clausius inequality

- Applying the energy balance to the combined system identified by dashed lines yields: $\delta W_C = \delta Q_R - dE_C$

- where δW_C is the total work of the combined system ($\delta W_{rev} + \delta W_{sys}$) and dE_C 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

- Since the cyclic integral of ene $W_C = T_R \oint \frac{\delta Q}{T}$

Clausius inequality

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

- Considering T_R 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.

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

Clausius inequality

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

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

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

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

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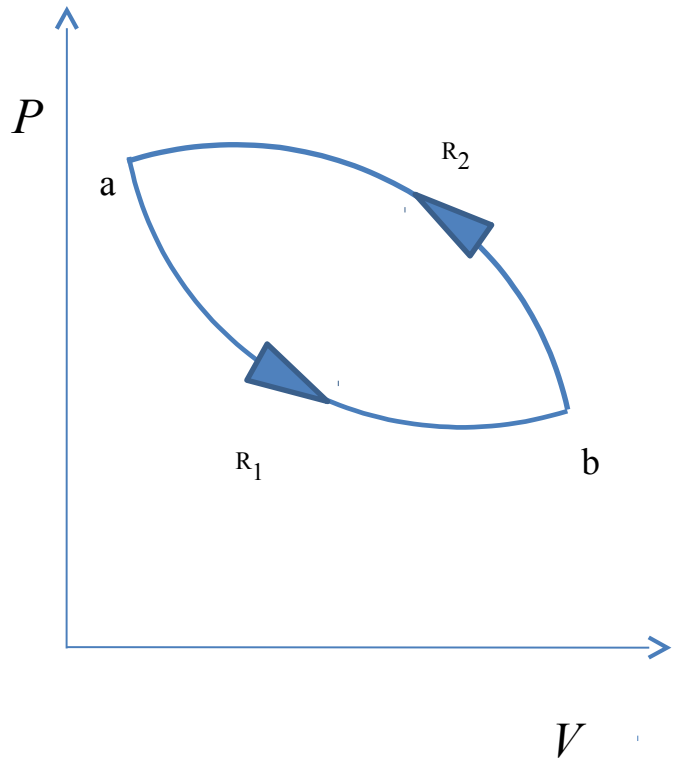
$$\oint_{R_1 R_2} \frac{dQ}{T} = 0$$

$$\int_a^b {}_{R_1} \frac{\delta Q}{T} + \int_b^a \frac{\delta Q}{T} = 0$$

or, $\displaystyle \int_a^b \frac{\delta Q}{T} = -\int_b^a \frac{\delta Q}{T}$

Since R_2 is a reversible path,

$$\int_a^b {}_{R_1} \frac{\delta Q}{T} = \int_a^b \frac{\delta Q}{T}$$

The property of entropy

- $\displaystyle\int_{a}^{b}{}_{R}\frac{\delta Q}{T}$ 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 $\displaystyle\int_{a}^{b}{}_{R}\frac{\delta Q}{T}$ is called entropy, denoted by S.

- When the two equilibrium states

$$\int_{a}^{b}{}_{R}\frac{\delta Q}{T} = S_b - S_a ;$$

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

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

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

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

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

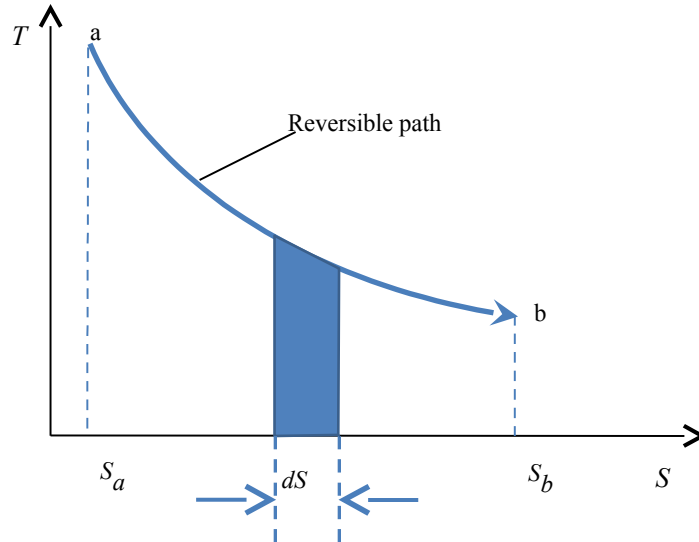If the process is reversible and adiabatic, $\delta Q_{rev} = 0$

$\therefore dS = 0 \quad or \quad S = \text{constant}$

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

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

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

Temperature-entropy plot

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

- 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.