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## ME 209 Basic Thermodynamics (Lecture-11)

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## Review of Lecture 10

- Understood the Carnot Corollary-I by which the reversible machines perform better than their irreversible counterparts operating between the same reservoirs
- Understood the Carnot corollary-II by which all the reversible machines perform equally well
- Thus, the heat transferred from reversible engines could be used as a thermometric sensor and a thermodynamic scale can be constructed
- Got exposed to an engine that works reversibly between two reservoirs (2-T reversible engine)

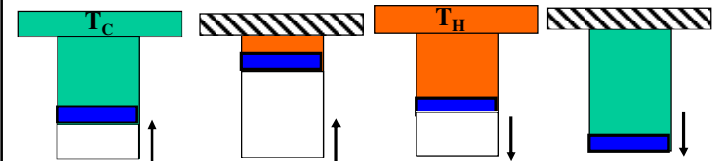
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## Agenda for Today

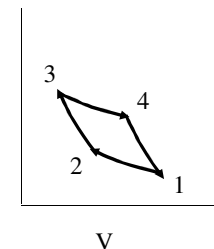
- Analyse a Carnot engine and show that the Thermodynamic scale and Ideal Gas Kelvin scale are identical
- Derive the Clausius Inequality, define entropy and entropy production
- Derive the Second law in terms of change of entropy for an infinitesimal process
- State the principle of increase in entropy of the universe.

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## Carnot Engine



1. Isothermal Compression (1-2)
2. Adiabatic Compression (2-3)
3. Isothermal Expansion (3-4)
4. Adiabatic Expansion (4-1)



### 5/16 Equivalence of Thermodynamic and Kelvin Scale-I

- Process 1-2 is a constant temperature process with  $T = T_C$ .

$$W_{12} = mRT_C \ln\left(\frac{V_2}{V_1}\right)$$

- Applying first law for the process 1-2 we get,

$$\Delta U = 0 = Q_{12} - W_{12}$$

$$\Rightarrow Q_{12} = W_{12} = mRT_C \ln\left(\frac{V_2}{V_1}\right) \quad \text{①}$$

- Similarly applying first law for the process 3-4 we get,

$$\Rightarrow Q_{34} = W_{34} = mRT_H \ln\left(\frac{V_4}{V_3}\right) \quad \text{②}$$

### 6/16 Equivalence of Thermodynamic and Kelvin Scale-II

- Process 2-3 is frictionless adiabatic process

$$\Rightarrow \frac{V_3}{V_2} = \left(\frac{T_2}{T_3}\right)^{\frac{1}{\gamma-1}} = \left(\frac{T_C}{T_H}\right)^{\frac{1}{\gamma-1}}$$

- Similarly for Process 4-1

$$\Rightarrow \frac{V_4}{V_1} = \left(\frac{T_1}{T_4}\right)^{\frac{1}{\gamma-1}} = \left(\frac{T_C}{T_H}\right)^{\frac{1}{\gamma-1}}$$

- From the above two equations,

$$\Rightarrow \frac{V_4}{V_1} = \frac{V_3}{V_2} \quad \Rightarrow \frac{V_4}{V_3} = \frac{V_1}{V_2} \quad \text{③}$$

### 7/16 Equivalence of Thermodynamic and Kelvin Scale-III

- From Eq. (1) in slide 3 of this lecture

$$Q_{12} = -Q_C = mRT_C \ln\left(\frac{V_2}{V_1}\right) \Rightarrow Q_C = mRT_C \ln\left(\frac{V_1}{V_2}\right) \quad \text{④}$$

- From Eq. (2) in slide 3 of this lecture, we have

$$Q_{34} = Q_H = mRT_H \ln\left(\frac{V_4}{V_3}\right) \quad \text{⑤}$$

- From Eqs. (3), (4) and (5) above, we have

$$\Rightarrow \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

### 8/16 Equivalence of Thermodynamic and Kelvin Scale-IV

- Previously we had shown that in thermodynamic scale

$$\Rightarrow \frac{Q_C}{Q_H} = \frac{\theta_C}{\theta_H}$$

- Thus  $\frac{T_C}{T_H} = \frac{\theta_C}{\theta_H}$  Or  $\frac{T}{T_{\text{ref}}} = \frac{\theta}{\theta_{\text{ref}}}$

- If  $T_{\text{ref}} = \theta_{\text{ref}}$ , then  $T = \theta$

- Thus, the thermodynamic scale and Kelvin scale are equivalent and Kelvin scale can be called absolute scale.

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### Carnot Efficiency/COP

$$\eta(\theta_H, \theta_C) = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

- This is the highest possible efficiency of an engine

$$COP_{REF} = \frac{Q_C}{Q_H - Q_C} = \frac{T_C}{T_H - T_C}$$

- This is the highest possible COP of a Refrigerator

$$COP_{HP} = \frac{Q_H}{Q_H - Q_C} = \frac{T_H}{T_H - T_C}$$

- This is the highest possible COP of a Heat Pump

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### Clausius Inequality-I

- Clausius Inequality lays foundation for the definition of quantitative description of II Law
- It states that for a cyclic process

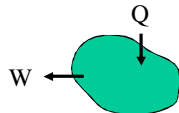
$$\oint \frac{dQ}{T} \leq 0$$

- The equality sign holds for a reversible cycle
- There are many ways to show this, let us follow Kelvin-Planck Route

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### Clausius Inequality-II

- Consider the system as shown having heat and work interaction with the surroundings during cyclic process

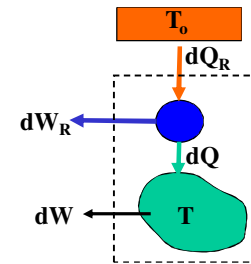


- For the purpose of analysis, we split the heat and work into a series of infinitesimal heat and work interaction
- It is assumed that all heat is added through an infinitesimal heat engine interacting with a reservoir

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### Clausius Inequality-III

- Note that in this thought experiment, a large number of cycles are executed by the reversible engine while our system executes one cycle



- For the cycle that the body executes

$$\oint_{\text{body}} dQ = \oint_{\text{body}} dW \quad \text{①}$$

- For the combined 1-T system

$$\oint_{\text{engine}} dW_R + \oint_{\text{body}} dW \leq 0 \quad \text{②}$$

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### Clausius Inequality-IV

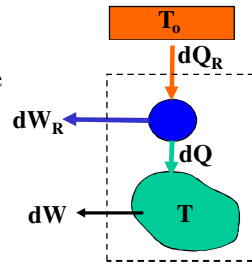
- If T is the body temperature during the infinitesimal process, then using Kelvin absolute scale for reversible engine

$$\frac{dQ_R}{T_o} = \frac{dQ}{T} \quad (3)$$

- First law for the reversible engine

$$dW_R = dQ_R - dQ$$

$$\Rightarrow dW_R = \frac{T_o}{T} dQ - dQ \quad (4)$$



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### Clausius Inequality-V

- Substituting Eq.(4) in Eq. (2), we get

$$\oint_{\text{body}} dW + \oint_{\text{body}} \frac{T_o}{T} dQ - \oint_{\text{body}} dQ \leq 0$$

- From Eq. (1), the cyclic work = cyclic heat for the body

$$\Rightarrow \oint_{\text{body}} \frac{T_o}{T} dQ \leq 0$$

$$\text{Or } \oint_{\text{body}} \frac{dQ}{T} \leq 0$$

Note that for a reversible process it is an equality

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### Entropy-I

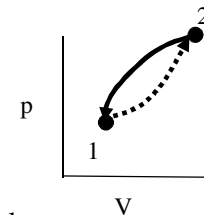
- We have just shown that  $\oint_{\text{reversible}} \frac{dQ}{T} = 0$
- This implies that we can write  $\frac{dQ_R}{T} = dS$
- Subscript R is chosen to represent reversible process
- In the above equation, S is a property and is called entropy

In classical thermodynamics, entropy is a mathematical entity and is as abstract as heat or momentum (mV) or moment of inertia (mK<sup>2</sup>). Its use needs to be understood and no time should be wasted on its physical interpretation

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### Entropy Production

- Let 1-2 be a irreversible process.
- Let us return to state 1 by a reversible process
- Since part of the cycle is irreversible,



$$\oint \frac{dQ}{T} < 0 \quad \text{or} \quad \oint \frac{dQ}{T} = -S_p \quad \text{Entropy production and is always positive}$$

$$\Rightarrow \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ_R}{T} = -S_p \quad \Rightarrow \int_1^2 \frac{dQ}{T} + \int_2^1 dS = -\int_1^2 dS_p$$

$$\Rightarrow \int_1^2 \frac{dQ}{T} - \int_1^2 dS = -\int_1^2 dS_p \quad \Rightarrow \int_1^2 dS = \int_1^2 \frac{dQ}{T} + \int_1^2 dS_p$$

## Second Law for Closed System

$$\int_1^2 dS = \int_1^2 \frac{dQ}{T} + \int_1^2 dS_p \quad \Rightarrow dS = \frac{dQ}{T} + dS_p$$

- The above expression is the second law for an infinitesimal process.
- It is very useful for deriving property relations

### Principle of increase in entropy of the universe

- For an isolated system  $dS$  is always positive as  $dQ = 0$  and  $dS_p$  is always positive