# Chapter 5 - Second Law of Thermodynamics

Lecture 16

Sections 5.7-5.8

MEMS 0051 Introduction to Thermodynamics

Mechanical Engineering and Materials Science Department
University of Pittsburgh

# Student Learning Objectives





At the end of the lecture, students should be able to:

- Define the absolute/thermodynamic temperature scale in general and for Ideal Gases

# Absolute Temperature Scale





- In relation to the **Zeroth Law of Thermodynamics**, we can define an **absolute temperature scale** that is independent of any property of matter
- The **thermodynamic temperature** (a.k.a. absolute temperature scale) is the absolute measure of temperature (in SI units), as defined by the 2$^{\text{nd}}$ and **3$^{\text{rd}}$ Law of Thermodynamics**
- The 3$^{\text{rd}}$ Law states the entropy of a perfect crystal is zero at absolute zero (i.e. at absolute zero, a material is at its minimum energy)

# Temperature and Carnot

- When we speak of the temperature of a system, we imply it is in thermal equilibrium
- When we analyze the Carnot cycle, the H.E. provides thermal communication between the high and low temperature reservoirs
- The H.E. directs $\dot{Q}_H$ from $T_H$ into the H.E., rejecting $\dot{Q}_L$ to $T_L$

# Relational Operator



- The second proposition of the Carnot cycle states two reversible H.E. operating between the same temperature reservoirs $T_H$ and $T_L$ have the same efficiency

$$\eta_{\text{Carnot}} = 1 - \frac{Q_L}{Q_H}$$

- That is, the efficiency is therefore a function of only temperatures

$$\implies \eta_{\text{Carnot}} = 1 - \psi(T_L, T_H)$$

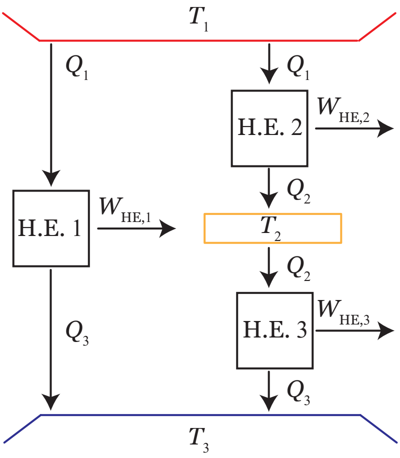
- $\psi$ is a functional relation operator

# Reversible Heat Engines





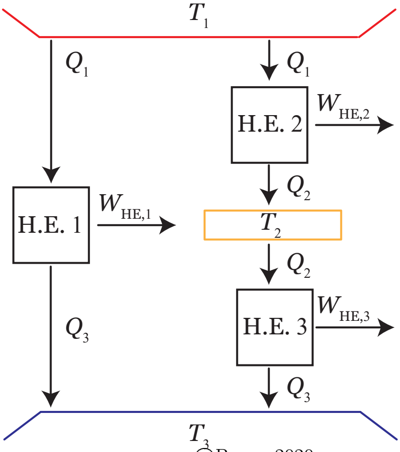
- Imagine we have a reversible H.E. operating between $T_1$ and $T_3$ (hot and cold)



# Reversible Heat Engines

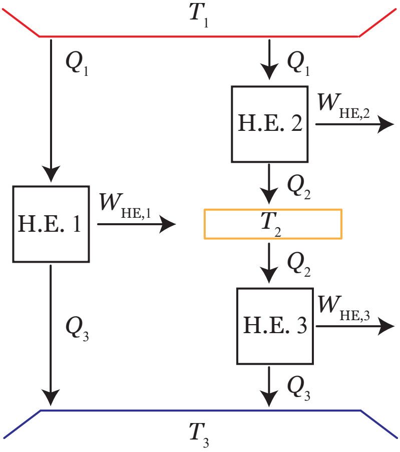


- Now we interject an intermediate temperature reservoir $T_2$, where $T_1 > T_2 > T_3$, and two reversible H.E., one between $T_1$ and $T_2$ and the other between $T_2$ and $T_3$



# Reversible Heat Engines

- The efficiency of the H.E. between $T_1$ and $T_3$ would be the same as one consisting of two cycles between $T_1$ and $T_2$ and $T_2$ and $T_3$




$$\eta_{\text{H.E.1}} = \frac{Q_1 - Q_3}{Q_1}$$

$$W_{\text{HE},2} = Q_1 - Q_2$$

$$W_{\text{HE},3} = Q_2 - Q_3$$

$$W_{\text{HE},2+3} = Q_1 - Q_3$$

$$\eta_{\text{HE},2+3} = \frac{W_{\text{HE},2+\text{HE},3}}{Q_1}$$

# Reversible Heat Engines



- Thus, the efficiency of the first heat engine between $T_1$ and $T_3$ is

$$\eta_{\text{HE},1} = 1 - \frac{Q_3}{Q_1} \implies \frac{Q_3}{Q_1} = \psi(T_1, T_3)$$

- The efficiency of the second set of heat engines uses $|Q_2|$, the magnitude of heat transferred

$$\eta_{\text{HE},2+\text{HE},3} = \frac{(Q_1 - |Q_2|) + (|Q_2| - Q_3)}{Q_1}$$

$$= \left(1 - \frac{|Q_2|}{Q_1}\right) + \left(1 - \frac{Q_3}{|Q_2|}\right)\left(\frac{|Q_2|}{Q_1}\right)$$

$$\implies \psi(T_2, T_3)\psi(T_1, T_2)$$

# Heat and Temperature

- Since the efficiency of the H.E. are equal

$$\psi(T_1, T_3) = \psi(T_2, T_3)\psi(T_1, T_2)$$

- We notice the LHS is not a function of $T_2$ although the RHS is
- Therefore, the product of the two terms in the RHS must eliminate $T_2$, and this is only achieved by using any monotonic function $g(T){=}T$

$$\psi(T_2, T_3) = \frac{g(T_3)}{g(T_2)}; \qquad \psi(T_1, T_2) = \frac{g(T_2)}{g(T_1)}$$

$$\psi(T_1, T_3) = \frac{g(T_3)}{g(T_1)}$$

# Carnot Efficiency





- Therefore, expressing $\psi$ in terms of $g(T)$, and choosing a reference $T$, we have an established temperature scale

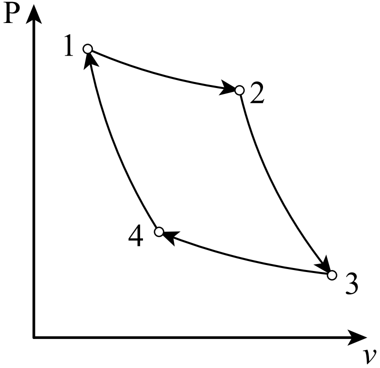
$$\frac{g(T_3)}{g(T_1)} = \frac{T_3}{T_1} = \frac{Q_3}{Q_1}$$

- Thus, the efficiency of the Carnot cycle can be expressed in terms of temperature

$$\boxed{\eta_{\text{Carnot}} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}}$$

# Ideal Gas

- Consider the Carnot cycle as shown on the $P$-$\nu$ diagram




- Recall the 4 individual processes (isothermal heat addition/rejection, reversible adiabatic compression/expansion)

# Ideal Gas





- The reversible work is given in terms of an Ideal Gas is

$$\delta w = P\,d\nu = \frac{RT}{\nu} d\nu$$

- The change of internal energy can be expressed as

$$du = C_{\forall O} dT$$

- Thus, the heat added to the system is

$$\delta q = du + \delta w = C_{\forall O} dT + \frac{RT}{\nu} d\nu$$

- Let's apply these equations to each of the four processes

# Ideal Gas





- Considering isothermal heat addition (1 to 2, $dT$=0)

$$\delta q = C_{\forall O} dT + \frac{RT}{\nu} d\nu \implies q_{1\rightarrow 2} = R\,T_H \ln\left(\frac{\nu_2}{\nu_1}\right)$$

- Considering adiabatic expansion (2 to 3, $q$=0)

$$0 = C_{\forall O} dT + \frac{RT}{\nu} d\nu \implies 0 = \int_{T_H}^{T_L} \frac{C_{\forall O}}{T} dT + R \ln\left(\frac{\nu_3}{\nu_2}\right)$$

$$\implies \int_{T_L}^{T_H} \frac{C_{\forall O}}{T} dT = R \ln\left(\frac{\nu_3}{\nu_2}\right)$$

# Ideal Gas



- Considering isothermal heat rejection (3 to 4, $dT$=0)

$$q_{3\rightarrow 4} = -RT_L \ln\left(\frac{\nu_4}{\nu_3}\right) = R\,T_L \ln\left(\frac{\nu_3}{\nu_4}\right)$$

- Considering adiabatic compression (4 to 1, $q$=0)

$$0 = C_{\forall O} dT + \frac{RT}{\nu} d\nu \implies 0 = \int_{T_L}^{T_H} \frac{C_{\forall O}}{T} dT + R \ln\left(\frac{\nu_1}{\nu_4}\right)$$

$$\implies \int_{T_L}^{T_H} \frac{C_{\forall O}}{T} dT = -R \ln\left(\frac{\nu_1}{\nu_4}\right)$$

# Ideal Gas



- We notice for the two adiabatic processes, we have the same integral (bounds and integrand)

$$\Longrightarrow \int_{T_L}^{T_H} \frac{C_{\forall O}}{T} dT = -R\ln\left(\frac{\nu_1}{\nu_4}\right) = R\ln\left(\frac{\nu_3}{\nu_2}\right)$$

- Dividing by $R$ and exponentiating, we obtain a useful relation of specific volumes

$$\frac{\nu_1}{\nu_4} = \frac{\nu_2}{\nu_3} \Longrightarrow \frac{\nu_3}{\nu_4} = \frac{\nu_2}{\nu_1}$$

# Ideal Gas



- Now, recalling the definition of the thermodynamic temperature scale, in particular, the ratio of heat rejected to input

$$\frac{Q_L}{Q_H} = \frac{q_{3\rightarrow 4}}{q_{1\rightarrow 2}} = \frac{R\,T_L \ln\left(\dfrac{\nu_3}{\nu_4}\right)}{R\,T_H \ln\left(\dfrac{\nu_2}{\nu_1}\right)} = \frac{T_L}{T_H}$$

- Thus, we have the same thermodynamic temperature scale for Ideal Gases.

# Student Learning Objectives





At the end of the lecture, students should be able to:

- Define the absolute/thermodynamic temperature scale in general and for Ideal Gases
  - The absolute temperature scale, i.e. the thermodynamic temperatures scale, is that of Kelvin. Using this scale, we can replace the quantity $Q_L/Q_H$ with $T_L/T_H$ in our formulation for efficiency.

# Suggested Problems

- 5.44, 5.45, 5.46, 5.52, 5.60, 5.65, 5.97, 5.98, 5.99