MME 231: Lecture 06

The Laws of Thermodynamics

The Second Law of Thermodynamics ….

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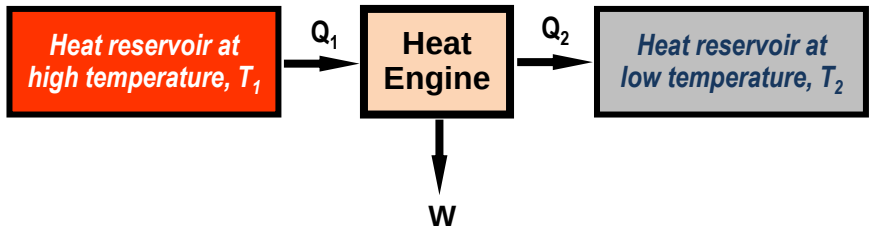
Today's Topics

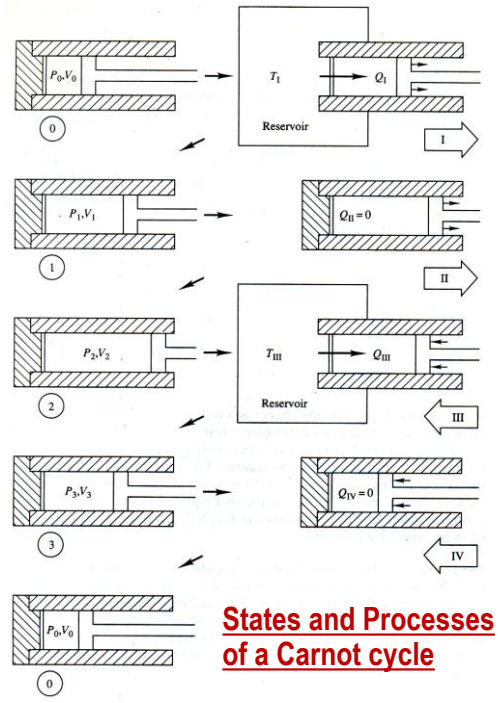
- Relation between entropy transfer and heat
- Entropy change for reversible and irreversible processes
- The work function
- Common non-mechanical works

Relation between Entropy Transfer and Heat

- **Sadi Carnot** (1824) – inventor of heat engines.



Schematic representation of the working principle of a heat engine



States and Processes of a Carnot cycle

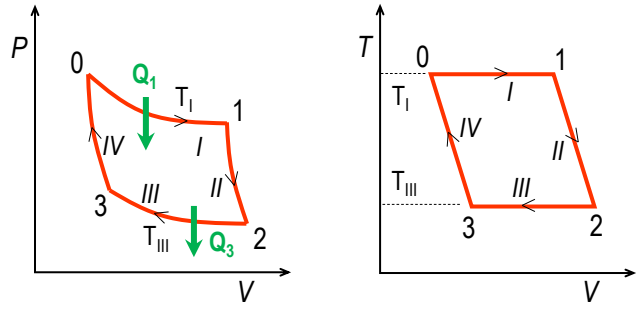
Process I: Superheated steam is passed from boiler (high temperature heat reservoir) to the cylinder using reversible isothermal process.

Process II: The steam performs work adiabatically by expanding against the piston. The temperature of the system (steam) is decreased.

Process III: The spent steam is exhausted isothermally to the atmosphere (low temperature heat reservoir).

Process IV: A fly wheel returns the piston adiabatically to its original position, thus completing the cycle and preparing for the next working stroke.

The Carnot Cycle



(a) **(b)**

The Carnot cycle in (a) P-V coordinate, and in (b) T-V coordinate.

The reversible paths used to complete the cycle 0-1-2-3-0 are:

I – isothermal expansion, *II – adiabatic expansion,*

III – isothermal compression *IV – adiabatic compression.*

■ The overall efficiency of heat engine

$$\eta = \frac{\textbf{Work obtained}}{\textbf{Heat input}} = \frac{\textbf{- W}}{\textbf{Q}_I} = \frac{\textbf{T}_I \textbf{ - T}_{III}}{\textbf{T}_I} \qquad (3.8)$$

W = total work done on the system (heat engine)
Q_I = heat absorbed by the system during stage I
T_I = temperature of hot reservoir
T_{III} = temperature of cold reservoir

■ Using the first law, for the overall cyclic process:

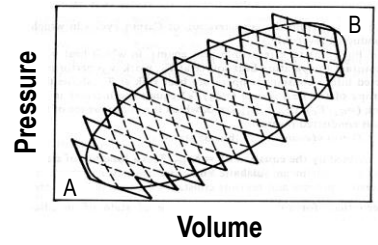
$\Delta U = 0 = W + Q_I + Q_{III}$ (using $W'=0$)

$$\textbf{W = - (Q}_I \textbf{ + Q}_{III}\textbf{)} \qquad (3.9)$$

- Substituting Eq.(3.9) into Eq.(3.8) will result

$$\frac{Q_I + Q_{III}}{Q_I} = \frac{T_I - T_{III}}{T_I}$$

$$\frac{Q_I}{T_I} + \frac{Q_{III}}{T_{III}} = 0$$



A cyclic process ABA broken into a large number of Carnot cycles

- For the overall cyclic path ABA,

$$\sum Q/T = 0 \qquad \oint \delta Q_{rev} / T = 0$$

- Thus, **Q/T** has the property of a **state function**.
  Clausius called this thermodynamic function as the **entropy** of the system, S.

- Thus, the relation between heat absorbed and entropy transfer into a system becomes

$$\Delta S = \frac{Q_{rev}}{T}$$

- For infinitesimal change of process

$$\delta Q_{rev} = TdS \; ; \quad Q_{rev} = \int TdS$$

$$\Delta S = \int dS = \int \frac{\delta Q_{rev}}{T}$$

Entropy Changes for Different Processes

- Since entropy is a state function, for the process A⇒B,

$$\Delta S_{rev}\,[A \rightarrow B] = \Delta S_{irr}\,[A \rightarrow B]$$

$$\Delta S_{rev,t} + \Delta S_{rev,p} = \Delta S_{irr,t} + \Delta S_{irr,p}$$

$$\Delta S_{irr,t} = \Delta S_{rev,t} - \Delta S_{irr,p}$$

$$\int \delta Q_{irr}/T < \int \delta Q_{rev}/T$$

- For an isothermal process, T is constant, and

$$[\,Q_{rev}\,]_T > [\,Q_{irr}\,]_T \qquad (3.14)$$

- For all possible isothermal processes:
  Heat absorbed by a reversible process is the maximum.

Example 3.2

A steel casting weighing 40 kg and at a temperature of 900 C is quenched in 2000 kg oil at 25 C.

If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together?

C_P (steel) = 0.5 kJ/kg-K ; C_P (oil) = 2.5 kJ/kg-K

Answer:

To determine the final equilibrium temperature of oil and steel, we balance the energies of oil and steel casting at T:

(40 kg) (0.5 kJ/kg-K) (T – 1173 K)

+ (2000 kg) (0.25 kJ/kg-K) (T – 298 K) = 0

T = 331.65 K

(a) During heating the amount of heat absorbed by a system can be calculating using $\delta_{Qrev} = m C_P dT$. Then

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta Q}{T} = \int_{T_1}^{T_2} \frac{mC_P dT}{T} = mC_P \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = (40\ \text{kg})\left(0.5\frac{\text{kJ}}{\text{kg-K}}\right) \ln\left(\frac{331.65\ \text{K}}{1173\ \text{K}}\right) = -25.26\ \text{kJ/K}$$

(b) Change in entropy of the oil

$$\Delta S = (2000\ \text{kg})\left(0.25\frac{\text{kJ}}{\text{kg-K}}\right) \ln\left(\frac{331.65\ \text{K}}{298\ \text{K}}\right) = +53.49\ \text{kJ/K}$$

(b) Total entropy change

$$\Delta S = -25.26 + 53.49 = 28.23\ \text{kJ/K}$$

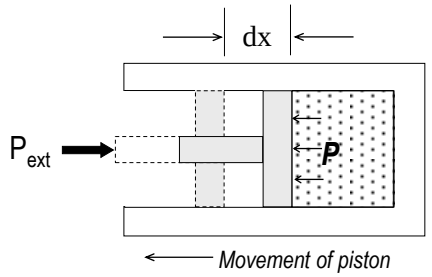
Note that although the entropy of the casting is decreased, total entropy change (for the oil and the steel casting) is increased.

The Work Function

- For a finite process, the work done is defined as:

$$W = \int \delta W = \int \mathbf{F(x)}\,.\,\mathbf{dx}$$

F = force
dx = displacement



$$\delta W = (P_{ext}\,.\,A)\,.\,(-dx)$$

$$\delta W = P_{ext}\,(-dV)$$

- For **reversible** expansion of the gas, the value of dP would be so small that for all practical purposes,

$$P_{ext} = P$$

- Thus, the work done on the system

$$\delta W_{rev} = - P\,dV$$

$$\delta W_{irr} = - P_{ext}\,dV$$

$$\delta W_{rev} = -PdV$$

$$W_{rev} = -\int PdV$$

- Since for irreversible processes, $P_{ext} < P$,
  work done by a reversible process is always the maximum.

Some Common Non-Mechanical Works

1. **Gravitational work,** $m_f h$
   where $\mathbf{m_f}$ is the force acting on the system and **h** the height to which the system is lifted against gravity.
2. **Electrical work,** EdQ
   where **E** is the potential difference and **dQ** the charge.
3. **Surface work,** γdA
   where γ is the surface tension and **A** the area.
4. **Centrifugal work,** $m\varpi^2 r$
   where **m** is the mass of the system, ϖ the angular velocity, and **r** the distance from axis of rotation.

Next Class

Lecture 07

The Combined Statement

Rashid/ Ch#3