

Chapter 20: Entropy and Second Law of Thermodynamics

(Fundamental of Physics, 10th edition)

- **Lecture-6:** Concept of entropy, Change in entropy for reversible and irreversible processes, related problems, Second law of thermodynamics in terms of entropy, entropy in the real world: engine, Carnot engine, and its working principles.

20-1 Irreversible process and entropy:

□ One-way (irreversible) processes:

- Processes can occur only in a certain sequence (the right way) and never in the reverse sequence (the wrong way). An egg is dropped onto a floor, a pizza is baked.
- These one-way processes are irreversible, meaning that they cannot be reversed by means of only small changes in their environment.
- The key to understanding why one-way processes cannot be reversed involves a quantity known as entropy.

□ Entropy postulate:

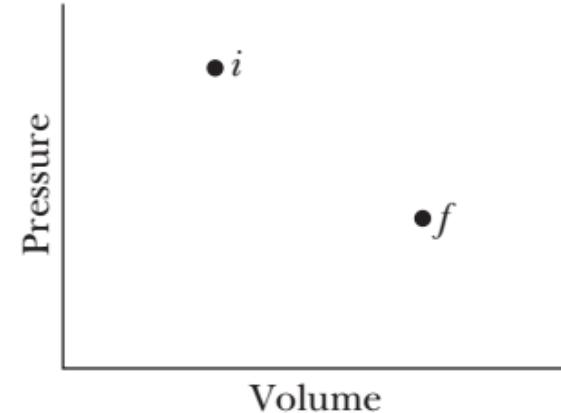
“If an irreversible process occurs in a closed system, the entropy S of the system always increases; it never decreases”. [$\Delta S > 0$]

- Entropy differs from energy in that entropy does not obey a conservation law. The energy of a closed system is conserved; it always remains constant. For irreversible processes, the entropy of a closed system always increases.

20-1 Change in entropy:

We define the change in entropy $S_f - S_i$ of a system during a process that takes the system from an initial state *i* to a final state *f* as

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$



Here **Q** is the energy transferred as heat to or from the system during the process, and **T** is the temperature of the system in kelvins. Thus, an entropy change depends not only on the energy transferred as heat but also on the temperature at which the transfer takes place. Because **T** is always **positive**, the **sign of ΔS** is the **same** as that of **Q**. The SI **unit** for entropy and entropy change is the **joule per kelvin**.

Reversible isothermal expansion:

$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{Q}{T}$$

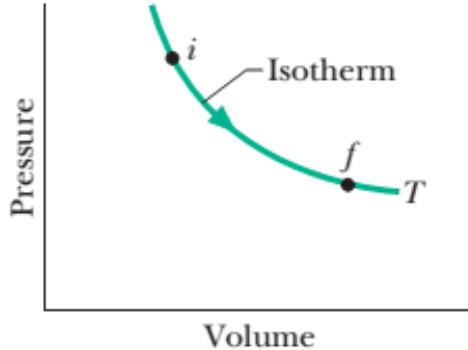
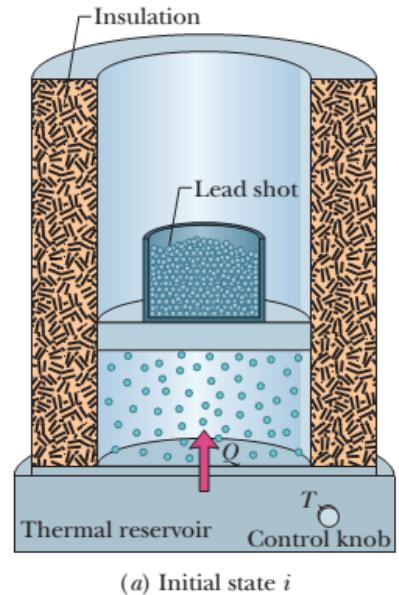


Figure 20-4 A p - V diagram for the reversible isothermal expansion of Fig. 20-3. The intermediate states, which are now equilibrium states, are shown.

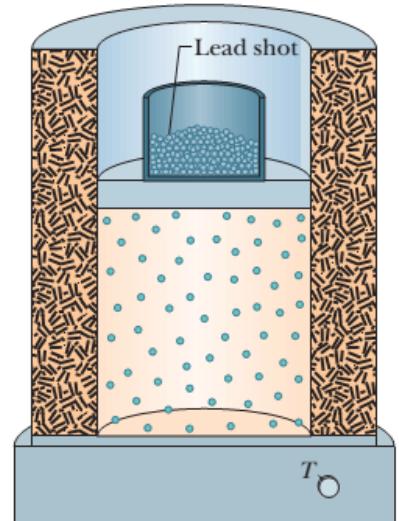
To keep the temperature T of the gas constant during the isothermal expansion, heat Q must have been energy transferred from the reservoir to the gas. Thus, Q is positive and the entropy of the gas increases during the isothermal process.

- To find the entropy change for an irreversible process, replace that process with any reversible process that connects the same initial and final states. Calculate the entropy change for this reversible process with

$$\Delta S = \int_i^f \frac{dQ}{T}.$$



↑
Reversible process



(b) Final state f

20-1 Entropy as a state function (state property):

We can prove that entropy is a **state function** for the special and important case in which an **ideal gas** is taken through a **reversible process**.

To make the process reversible, it is done slowly in a series of small steps, with the gas in an equilibrium state at the end of each step. For each small step, the energy transferred as **heat to or from the gas is dQ** , the work done by the gas is **dW** , and the change in internal energy is **dE_{int}** .

First law of thermodynamics, $dE_{int} = dQ - dW$

$$dQ = dW + dE_{int}$$

We know, for reversible process $dW = p dV$

$$dE_{int} = nC_v dT$$

$$dQ = p dV + nC_v dT$$

Ideal gas law, $pV = nRT$ $\therefore p = \frac{nRT}{V}$

$$dQ = \frac{nRT}{V} dV + nC_v dT$$

$$\frac{dQ}{T} = nR \frac{dV}{V} + nC_v \frac{dT}{T}$$

Integrating each term between an arbitrary initial state i and an arbitrary final state f ,

$$\int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f nC_v \frac{dT}{T}$$

$$\Delta S = nR[\ln V]_i^f + nC_v[\ln T]_i^f$$

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

Thus, the change in entropy ΔS between the initial and final states of an ideal gas depends only on properties of the initial state (V_i and T_i) and properties of the final state (V_f and T_f); ΔS does not depend on how the gas changes between the two states.

Sample Problem 20.02: Suppose 1.0 mol of nitrogen gas is confined to the left side of the container of Fig. 20-1a. You open the stopcock, and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process?

Solution:

Here, $n = 1 \text{ mol}$

$$V_i = V$$

$$V_f = 2V$$

$$T_i = T_f$$

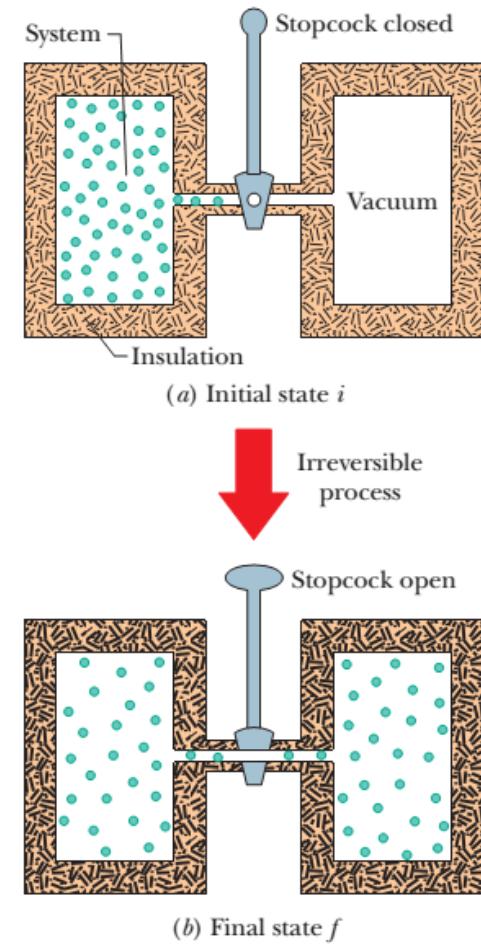
$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_f}$$

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln 1$$

$$\Delta S = nR \ln \frac{V_f}{V_i} + 0$$

$$\begin{aligned}\Delta S &= nR \ln \frac{V_f}{V_i} = 1.0(8.31) \ln \frac{2V}{V} \\ &= 1.0(8.31) \ln 2 \\ &= 5.76 \text{ J/K}\end{aligned}$$



2. An ideal gas undergoes a reversible isothermal expansion at 77.0 °C, increasing its volume from 1.30 L to 3.40 L. The entropy change of the gas is 22.0 J/K. How many moles of gas are present?

Solution:

$$\text{Here, } T_i = T_f = 77^\circ\text{C} = (77 + 273) \text{ K} = 350 \text{ K} \quad V_i = 1.30 \text{ L} \quad V_f = 3.40 \text{ L}$$

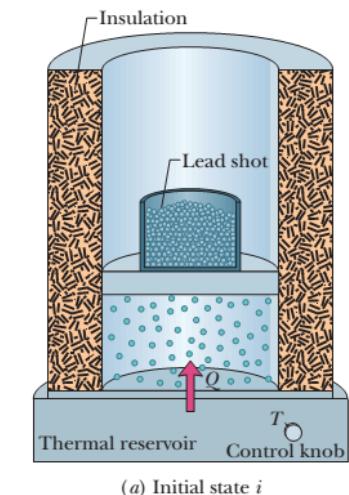
$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{350}{350}$$

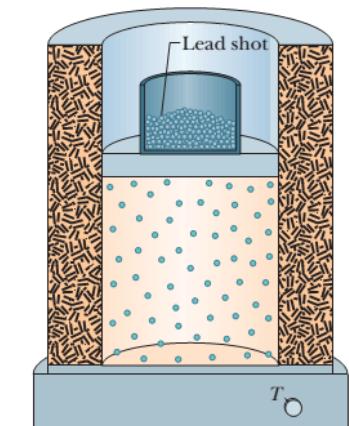
$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln 1$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$n = \frac{\Delta S}{R \ln \frac{V_f}{V_i}} = \frac{22}{8.31 \{ \ln \left(\frac{3.40}{1.30} \right) \}} = 2.754 \text{ mol}$$



(a) Initial state i



(b) Final state f

Problems for Practice: Homework

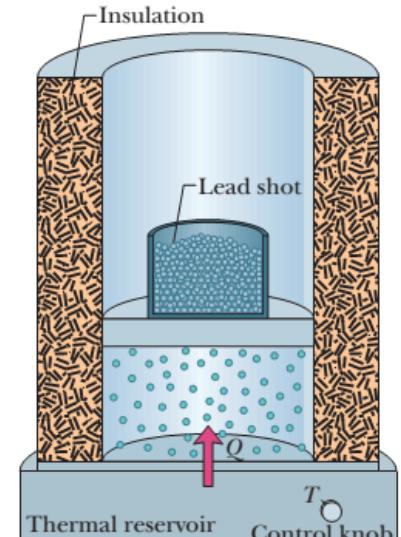
- 3. A 2.50 mol sample of an ideal gas expands reversibly and isothermally at 360 K until its volume is doubled. What is the increase in entropy of the gas?**

- 4. How much energy must be transferred as heat for a reversible isothermal expansion of an ideal gas at 132 °C if the entropy of the gas increases by 46.0 J/K?**

20-1 Second Law of Thermodynamics in terms of Entropy: $\Delta S \geq 0$

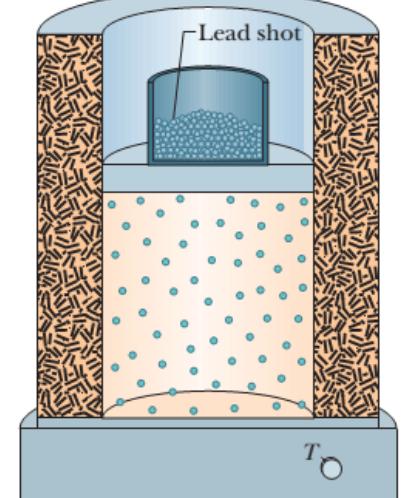
Reversible process: Let's check the change in entropy of the **enlarged system** consisting of **gas** and **reservoir**. We can then **calculate separately** the **entropy changes** from the following equations.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{Q}{T} \quad T = \text{constant}$$



(a) Initial state *i*

↑
Reversible process
↓



(b) Final state *f*

$$\Delta S_{gas} = -\frac{Q}{T}$$

$$\Delta S_{res} = +\frac{Q}{T}$$

$$\Delta S = -\frac{Q}{T} + \frac{Q}{T} = 0$$

“If a process occurs in a **closed system**, the entropy of the system **increases for irreversible processes ($\Delta S > 0$)** and **remains constant for reversible processes ($\Delta S = 0$)**. It **never decreases**.”

That is, $\Delta S \geq 0$

- In the **real world almost all processes are irreversible** to some extent because of friction, turbulence, and other factors, so the entropy of real closed systems undergoing real processes always increases. Processes in which the system's entropy remains constant are always idealizations.

20-2 Entropy in the Real World: Engines

Heat Engine: A heat engine, or more simply, **an engine**, is a device that **extracts energy from its environment** in the form of **heat and does useful work**. At the **heart of every engine** is a **working substance**.

Carnot Engine: Although **an ideal gas does not exist**, any **real gas approaches ideal behavior if its density is low enough**. Similarly, we can **study real engines** by analyzing the behavior of an **ideal engine (Carnot Engine)**.

“An ideal engine where all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence”.

Schematic of a Carnot engine

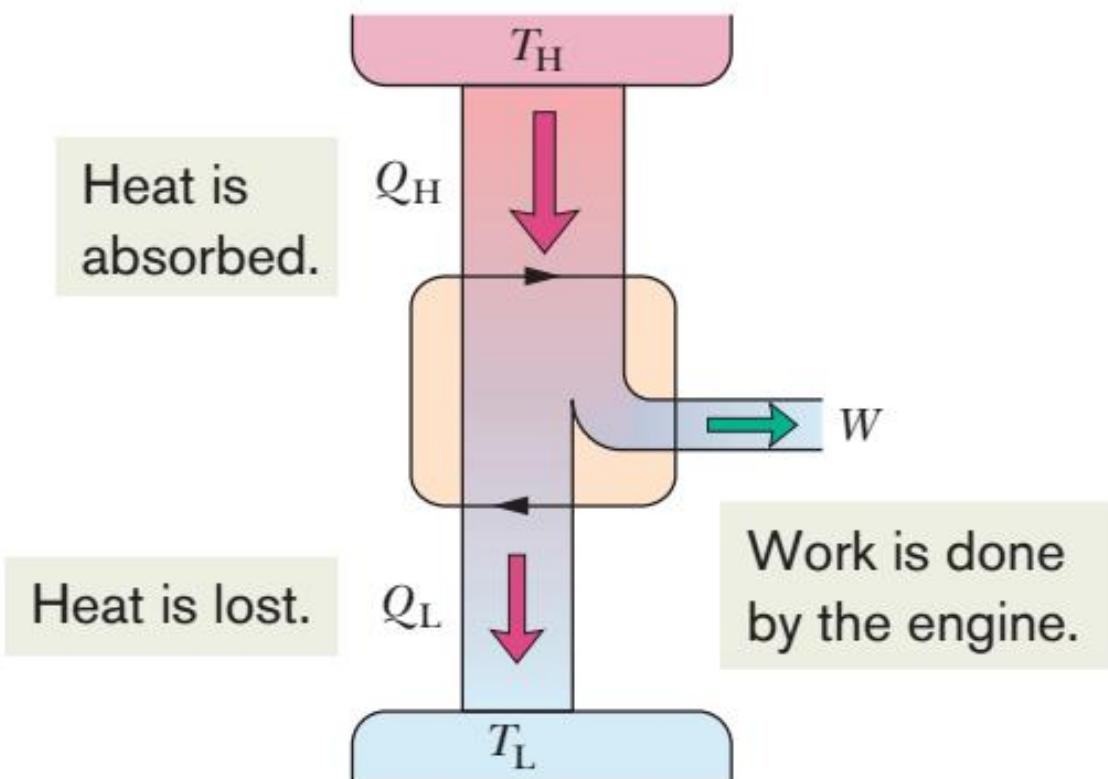
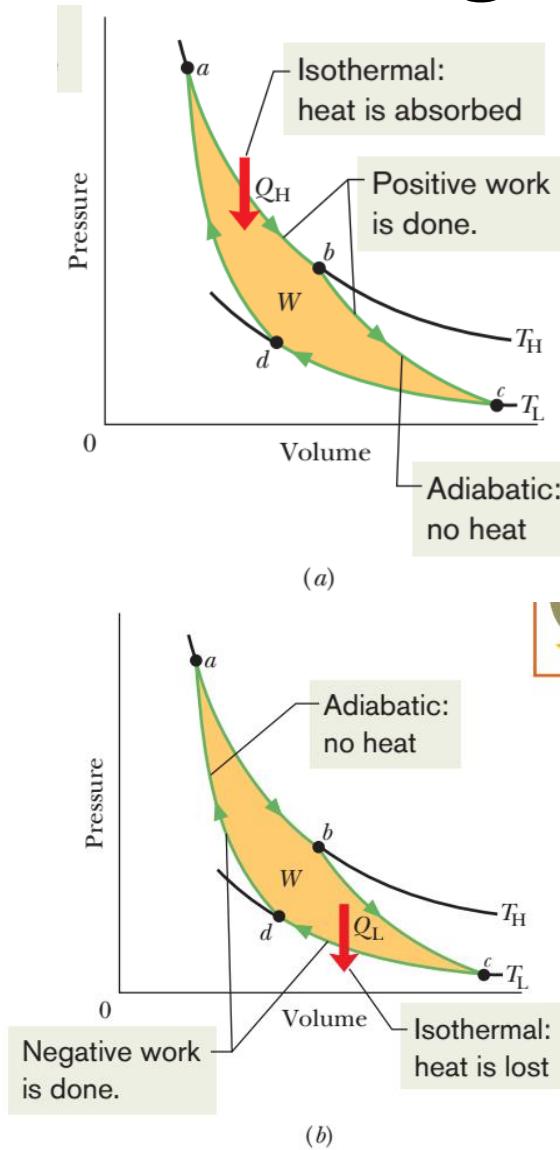


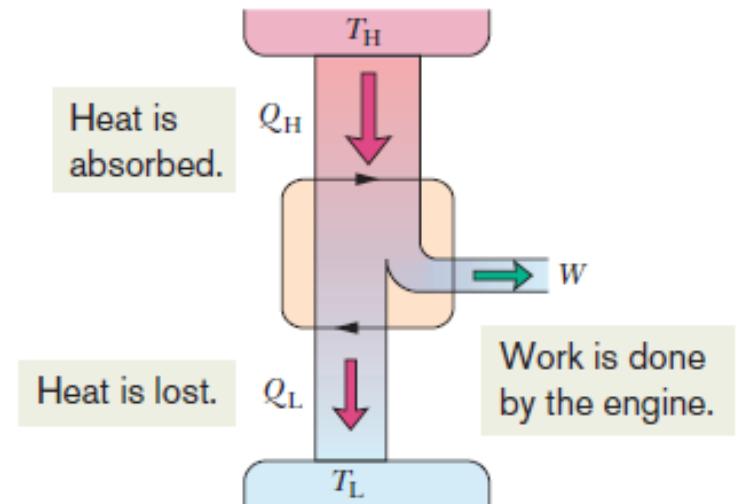
Figure 20-8 The elements of a Carnot engine. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a p - V plot. Energy $|Q_H|$ is transferred as heat from the high-temperature reservoir at temperature T_H to the working substance. Energy $|Q_L|$ is transferred as heat from the working substance to the low-temperature reservoir at temperature T_L . Work W is done by the engine (actually by the working substance) on something in the environment.

pV diagram of a Carnot Engine

Figure 20-9 A pressure–volume plot of the cycle followed by the working substance of the Carnot engine in Fig. 20-8. The cycle consists of two isothermal (*ab* and *cd*) and two adiabatic processes (*bc* and *da*). The shaded area enclosed by the cycle is equal to the work W per cycle done by the Carnot engine.



Schematic of
a Carnot engine



The Work:

In a Carnot engine, the working substance completes reversible cycles. Thus for a complete cycle of the working substance, the net internal energy change,

$$\Delta E_{int} = 0$$

In each cycle of a Carnot engine, the heat Q_H is transferred to the working substance from the high temperature reservoir T_H and the heat Q_L is transferred from the working substance to the low temperature reservoir T_L .

So, the net heat transfer per cycle,

$$Q = |Q_H| - |Q_L|$$

The first law of thermodynamics for the Carnot cycle, $\Delta E_{int} = Q - W$

$$0 = Q - W$$

$$W = Q$$

$$W = |Q_H| - |Q_L|$$

This is the net work done by a Carnot engine during a cycle.

Entropy Changes:

There are two isothermal processes in each cycle of a Carnot engine.

- During the isothermal expansion, the working substance absorbs heat $|Q_H|$ at temperature T_H .

The increase in entropy, $\Delta S_H = \frac{+|Q_H|}{T_H}$

- Again, during the isothermal compression, the working substance releases heat $|Q_L|$ at constant temperature T_L .

The decrease in entropy, $\Delta S_L = \frac{-|Q_L|}{T_L}$

- The net entropy change per cycle,
- For a complete cycle, $\Delta S = 0$

$$\Delta S = \Delta S_H + \Delta S_L$$

$$\Delta S = \frac{+|Q_H|}{T_H} + \frac{-|Q_L|}{T_L}$$

$$0 = \frac{+|Q_H|}{T_H} + \frac{-|Q_L|}{T_L}$$

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}$$

Efficiency of a Carnot Engine:

Thermal efficiency of any engine is defined as,

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we provide}} = \frac{|W|}{|Q_H|}$$

$$\varepsilon = \frac{|Q_H| - |Q_L|}{|Q_H|}$$

➤ $\varepsilon = 1 - \frac{|Q_L|}{|Q_H|}$ [any engine]

➤ $\varepsilon = 1 - \frac{T_L}{T_H}$ [Carnot engine] $[T_L < T_H]$

- Because $T_L < T_H$, the efficiency of Carnot engine is less than unity or less than 100%. Thus, only a **part** of the extracted heat is available to do **work** and the **rest** is delivered to the low temperature **reservoir**.

23. A Carnot engine whose low-temperature reservoir is at 17 °C has an efficiency of 40%. By how much should the temperature of the high-temperature reservoir be increased to increase the efficiency to 50%?

Solution:

Given,

$$T_L = 17^\circ\text{C} = 290 \text{ K}$$

Initial efficiency, $\varepsilon_c = 40\%$

Final efficiency, $\varepsilon'_c = 50\%$

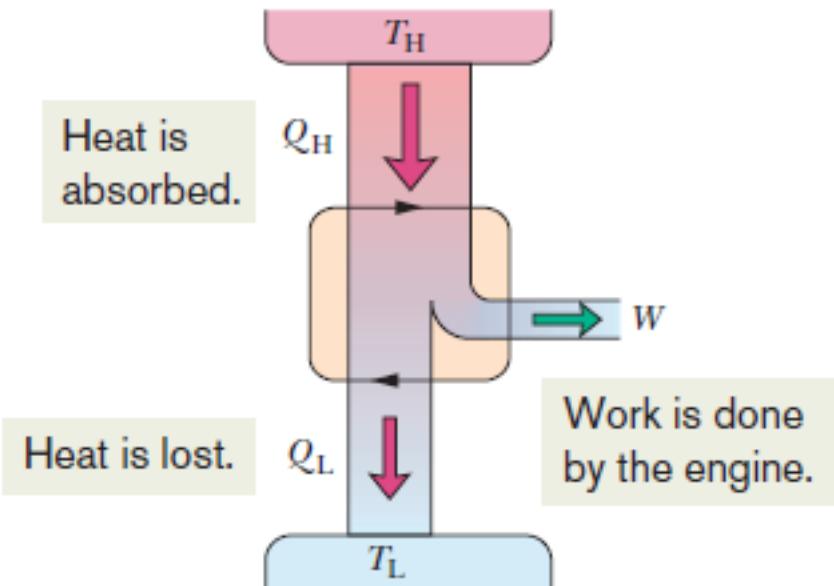
$$\Delta T_H = ?$$

For the initial state,

$$\varepsilon_c = 1 - \frac{T_L}{T_H}$$

$$\Rightarrow 40\% = 1 - \frac{T_L}{T_H}$$

Schematic of
a Carnot engine



$$\Rightarrow \frac{T_L}{T_H} = 1 - 0.40$$

$$\therefore T_H = 483.33 K$$

For the final state,

$$\varepsilon'_c = 1 - \frac{T_L}{T_{H'}}$$

$$\Rightarrow 50\% = 1 - \frac{T_L}{T'_H}$$

$$\Rightarrow \frac{T_L}{T'_H} = 1 - 0.50$$

$$\therefore T'_H = 580 K$$

So the increased temperature of the high temperature reservoir,

$$\Delta T_H = T'_H - T_H$$

$$= (580 - 483.33) K$$

$$= 96.67 K$$

24. A Carnot engine absorbs 52 kJ as heat and exhausts 36 kJ as heat in each cycle. Calculate (a) the engine's efficiency and (b) the work done per cycle in kilojoules.

Solution:

Given,

$$|Q_H| = 52 \text{ kJ} = 52 \times 10^3 \text{ J}$$

$$|Q_L| = 36 \text{ kJ} = 36 \times 10^3 \text{ J}$$

$$(a) \varepsilon_c = ?$$

We know,

$$\varepsilon_c = \left(1 - \frac{|Q_L|}{|Q_H|} \right) \times 100\%$$

$$= \left(1 - \frac{36 \times 10^3}{52 \times 10^3} \right) \times 100\%$$

$$= 30.77 \%$$

$$(b) W = ?$$

We know

$$W = |Q_H| - |Q_L| \\ = 52 \text{ kJ} - 36 \text{ kJ}$$

$$W = 16 \text{ kJ}$$

Schematic of a Carnot engine

