Chapter 20 Entropy and the second law of Thermodynamics

- **Irreversible process**

  is one that cannot be reversed by means of small changes in the environment.

  e.g. Broken egg can not go back to whole egg. Heat does not transfer from cold hand to hot coffee mug even though it would not violate the law of energy conservation.

- **The direction is set by a quantity called entropy**

  If an irreversible process occurs in a closed system, the entropy S of the system always increases, it never decreases. (entropy postulate)

- **Define the change in entropy to be:**

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

Q: energy transferred as heat

T: temperature in **Kelvins**

sign of ΔS and Q,   SI unit of S: J/K

- **Entropy is a state property**. It does not depend on the process, only depend on the initial and final states.

  Which of the followings are state properties: Q, T, V, W, P, E_{int}?

Check point 21-1: Water is heated on a stove. Rank the entropy changes of the water as its temperature rises from

(a) from 20^{o}C to 30^{o}C,

(b) from 30^{o}C to 35^{o}C,

(c) from 80^{o}C to 85^{o}C,

greatest first.

The second law of thermodynamics

- For the free expansion, we have $\Delta S > 0$. It is an irreversible process in a closed system.

- For the reversible isothermal process, for the gas $\Delta S > 0$ for expansion and $\Delta S < 0$ for compression. However, the gas itself is not a closed system. It is only a closed system if we include both the gas and the reservoir.

  during expansion:

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

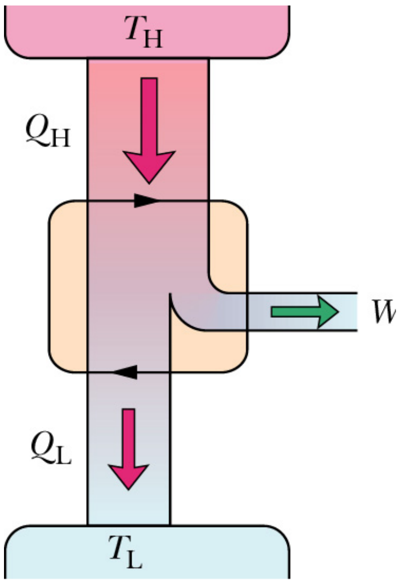
  So: $\Delta S_{total} = 0$

- If a process occurs in a *closed* system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

$$\Delta S \geq 0 \quad \text{(second law of thermodynamics)}$$

Entropy in real world: Engines

- An heat engine is a device that extract heat from its environment and does useful work.
  - Working substance
  - Strokes



- We will use ideal engine to study a real engine: In an ideal engine, all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence. We will treat the gas as ideal gas also.

Carnot Engine: one type of ideal engines.

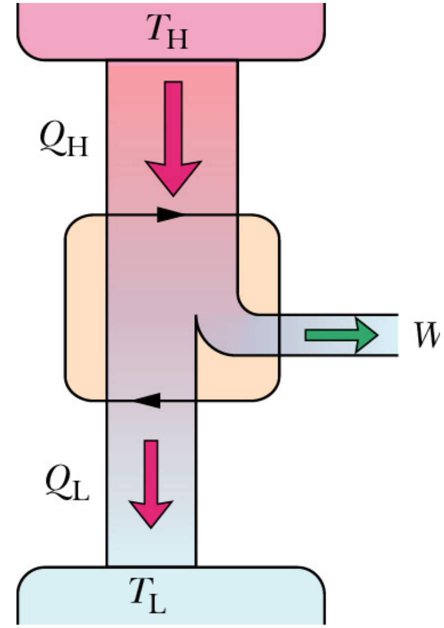
- **The cycle consists of four processes:**

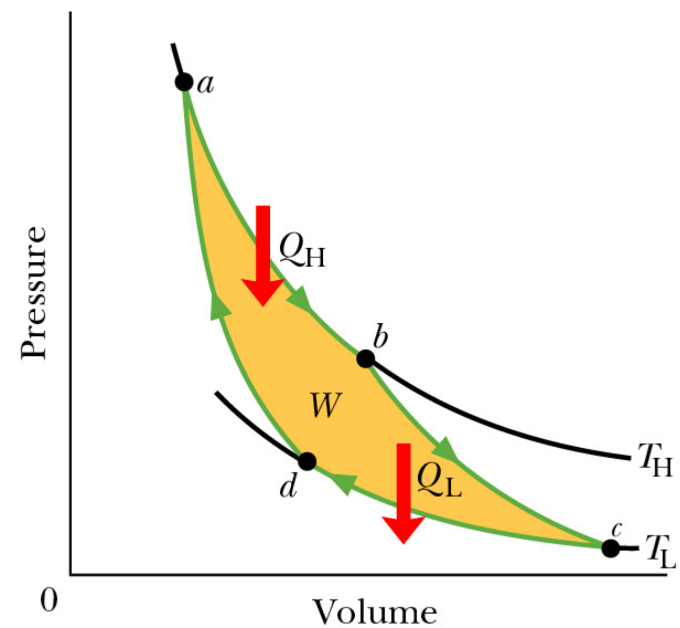
  a-b: isothermal expansion, working substance get heat Q_H from the high-temperature reservoir

  b-c**:** adiabatic expansion. Q = 0

  c-d: isothermal compression, working substance give heat Q_L to the low temperature reservoir

  d-a: adiabatic compression. Q = 0



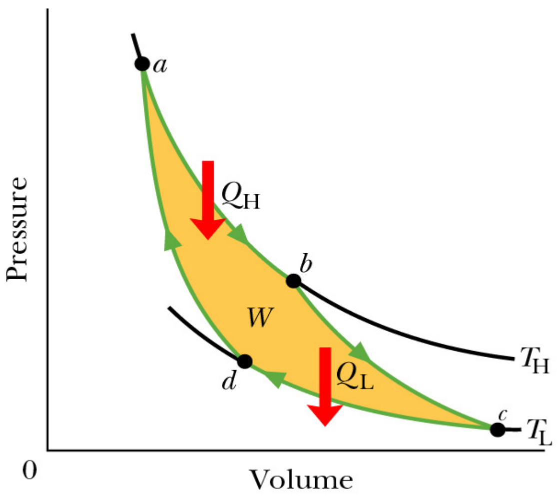


- **The work done by the working substance**:

  a-b-c: positive work

  c-d-a: negative work

  – Net work done in one cycle: area enclosed by cycle *abcda*.



- For a complete cycle, $\Delta E_{int} = 0$ (since E_{int} is a state function) that is: $Q - W = 0$, since $Q = |Q_H| - |Q_L|$

  Therefore: $W = Q = |Q_H| - |Q_L|$

- For a complete cycle, $\Delta S = 0$ (since S is a state function.)

- **Thermal efficiency of an engine**:

$$\varepsilon = \frac{energy\ we\ get}{energy\ we\ pay\ for} = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

- **For Carnot engine**: since the process is **reversible**, for the closed system(high-T reservoir + work substance + low-T reservoir), ΔS = 0 (2nd law of thermodynamics)

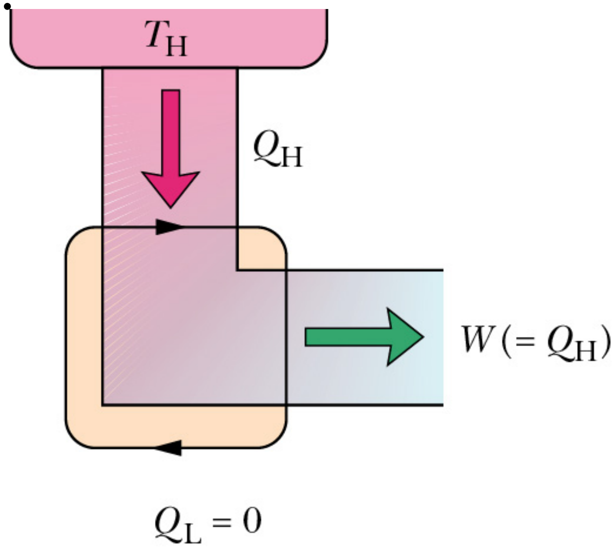
$$-\frac{|Q_H|}{T_H} + 0 + \frac{|Q_L|}{T_L} = 0 \qquad \frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H} \qquad \varepsilon = 1 - \frac{T_L}{T_H}$$

- **For real engine**: since the process is **irreversible**, ΔS > 0

$$-\frac{|Q_H|}{T_H} + 0 + \frac{|Q_L|}{T_L} > 0 \qquad \frac{|Q_L|}{|Q_H|} > \frac{T_L}{T_H} \qquad \varepsilon < (1 - \frac{T_L}{T_H})$$

- Is **perfect engine**, which converts all Q_H to work so that $Q_L = 0$ and $\varepsilon = 1$, possible?

The entropy change for the closed system:



$$\Delta S = -\frac{|Q_H|}{T_H} + 0 + 0 = -\frac{|Q_H|}{T_H} < 0$$

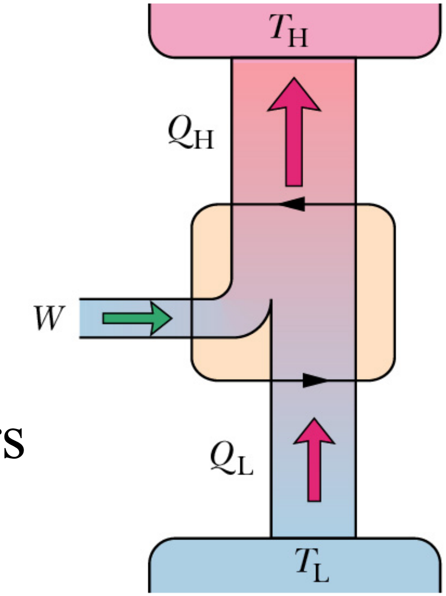
violates the 2nd law of thermodynamics.

Also, for $\varepsilon = 1$, we need $T_L = 0$ or T_H to be infinity. That is impossible.

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

Refrigerators

- A refrigerator(or air conditioner, or heat pumps) is a device that uses work to transfer energy from a low-T reservoir to a high-T reservoir.



- Coefficient of performance for refrigerator

$$K = \frac{what\ we\ want}{what\ we\ pay\ for} = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|} = \frac{1}{|Q_H|/|Q_L| - 1}$$

- For a closed system (high-T and low-T reservoirs plus working substance), ΔS >= 0

$$\frac{|Q_H|}{T_H} + 0 - \frac{|Q_L|}{T_L} \geq 0 \qquad \frac{|Q_H|}{|Q_L|} \geq \frac{T_H}{T_L} \qquad K \leq \frac{1}{T_H/T_L - 1} = \frac{T_L}{T_H - T_L}$$

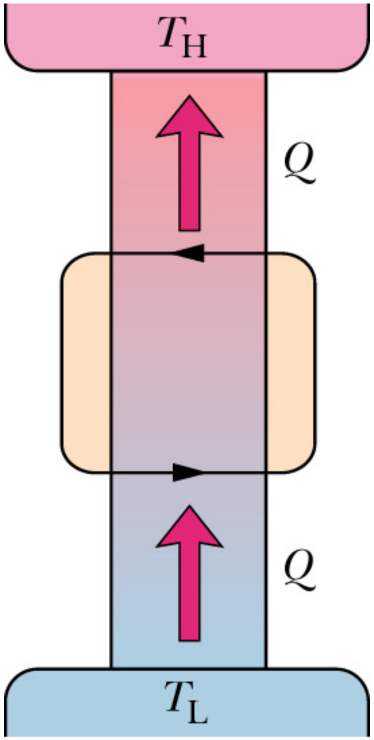
"=" : the ideal (Carnot) refrigerator. "<" : the real refrigerator.

- Is **perfect refrigerator**, which transfers heat from a cold reservoir to a warm reservoir without the need for work, possible?

  The entropy change for the closed system:

$$\Delta S = -\frac{|Q|}{T_L} + 0 + \frac{|Q|}{T_H} = |Q|\left(\frac{1}{T_H} - \frac{1}{T_L}\right) < 0$$

  violates the 2nd law of thermodynamics.



Sample 21-3, similar to web hw 15-5. Imagine a Carnot engine that operates between the temperatures $T_H = 850K$ and $T_L = 300$ K, The engine performs 1200 J of work each cycle, which takes 0.25 s

(a) what is the efficiency of this engine?

(b) what is the average power of this engine?

(c) how much heat is extracted from the high-T reservoir each cycle?