Chapter 20

- The Second Law of Thermodynamics

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Learning Goals

- Reversible and irreversible processes.
- The physics of internal-combustion engines*.
- Other thermodynamic systems: heat engines, fridges.
  - Performance and efficiency.
- The 2^{nd} law of thermodynamics and limiting efficiency.
- Entropy and what it leads to.

Introduction

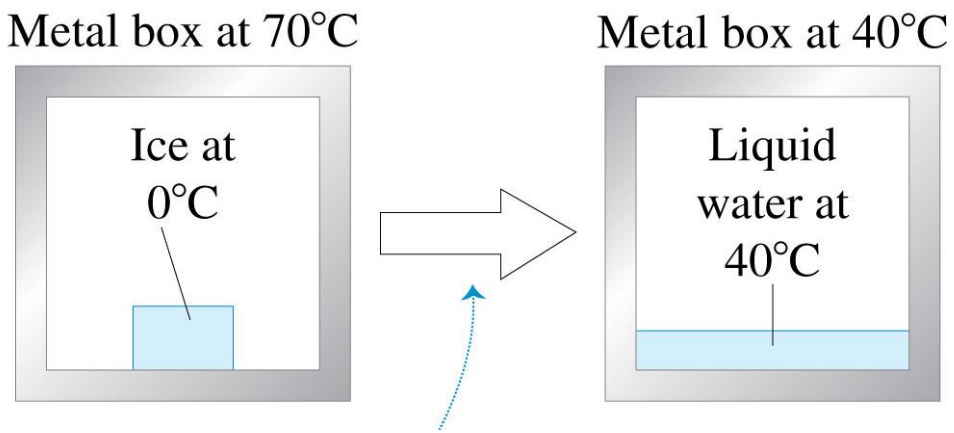
- When a volcano erupts, heat flows from the hot lava into the cool water.
  - Could heat flow the other way?
- Another point: we can convert mechanical energy completely into heat (using a car's brakes).
  - Can we convert heat completely into mechanical energy?
- The directions of thermodynamic processes are important and they create limitations.
  - This is the basis of the **second law of thermodynamics**.

Directions of thermodynamic processes

- In nature, thermodynamics processes are **irreversible**, they proceed spontaneously in only one direction.
  - Flow of heat from hot to cold body, free expansion, etc…
  - Sliding a book across a table (mech. energy into heat).

- Consider a metal box at 70°C filled with ice.

- Preferred directions for such processes are determined by the second law. (to be described later).

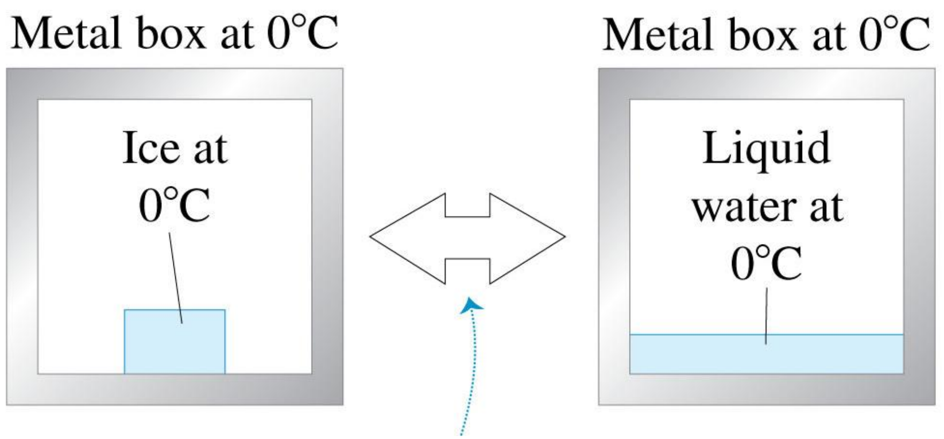


Directions of thermodynamic processes

- Imagine the same process but in a box at $0°\text{C}$. By reducing the temperature by *tiny* amount (ie, to $-0.0\ldots001°\text{C}$) we can **reverse** the process (liquid to ice).

- The system must be *very close* to thermal equilibrium within itself and its surroundings.

- This is an *idealized* system (ie. impossible) where no heat or work is exchanged.

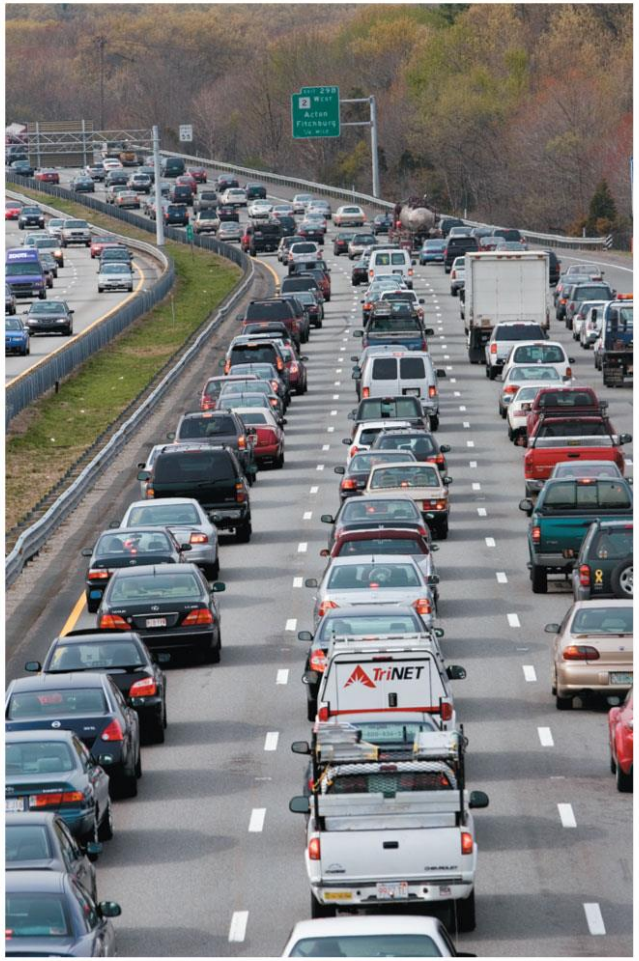


Disorder and thermodynamic processes

- Irreversible thermodynamic processes lead to more *disorder* or *randomness* (ie. converting mechanical energy into heat).
- The second law also introduces association with energy/heat/work and **entropy**.
- To introduce second law, we consider two classes of thermodynamic devices:
  - 1) <u>Heat engines</u> that convert heat into work.
  - 2) <u>Refrigerators</u> that transport heat from cooler to hotter bodies . (with input of work).

Heat engines

- A **heat engine** is any device that partially transforms *heat into work* or mechanical energy.
- Examples: any automobile engine (except EV), human body, steam engine, toy drinking bird.
- Sources: burning fossil fuels (coal, oil, gas) and nuclear reactions.
- Compare to "natural" mechanical energy sources like water/wind.



Heat engines

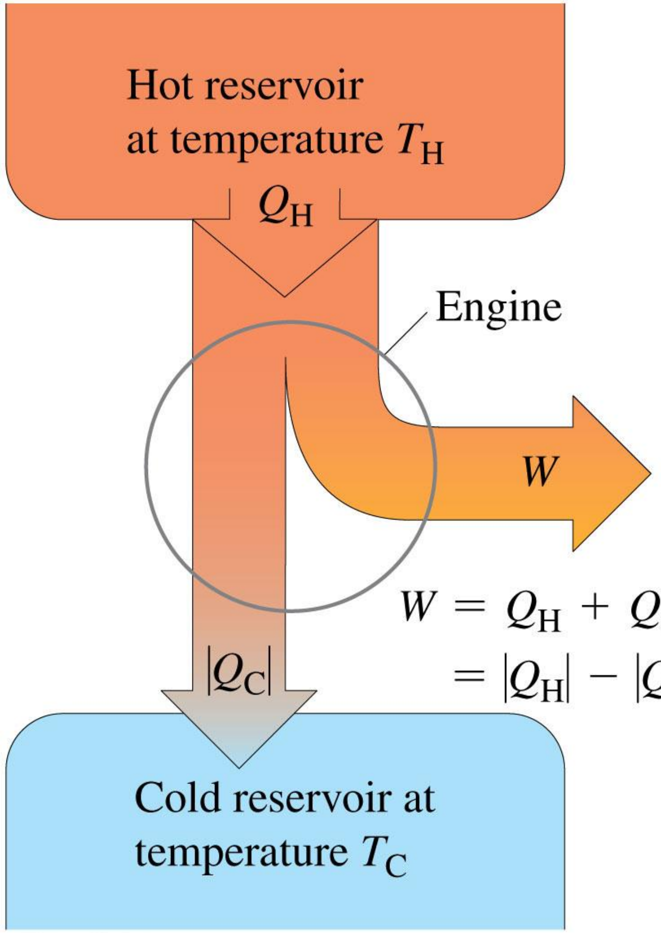
- **Heat engines** work on a *cyclic* process:
  $\Delta U = 0 \quad \rightarrow \quad Q = W$

- Heat (Q_H) is absorbed from a hot reservoir, part is transformed into work (W) and part is dumped into a cold reservoir (Q_C).

- The net heat absorbed is equal to the work:
  $Q = W = Q_H + Q_C = |Q_H| - |Q_C|$

- The **thermal efficiency** is:

$$\boxed{e} = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = \boxed{1 - \left|\frac{Q_C}{Q_H}\right|}$$



Ex. 20.1 – Analyzing a heat engine

- A gasoline truck engine takes in 10 kJ of heat and delivers 2 kJ of mechanical work per cycle. The heat is obtained by burning gasoline with heat of combustion $L_C = 5 \times 10^4$ J/g.

  (a) What is the thermal efficiency in each cycle?

  (b) How much heat is discarded in each cycle?

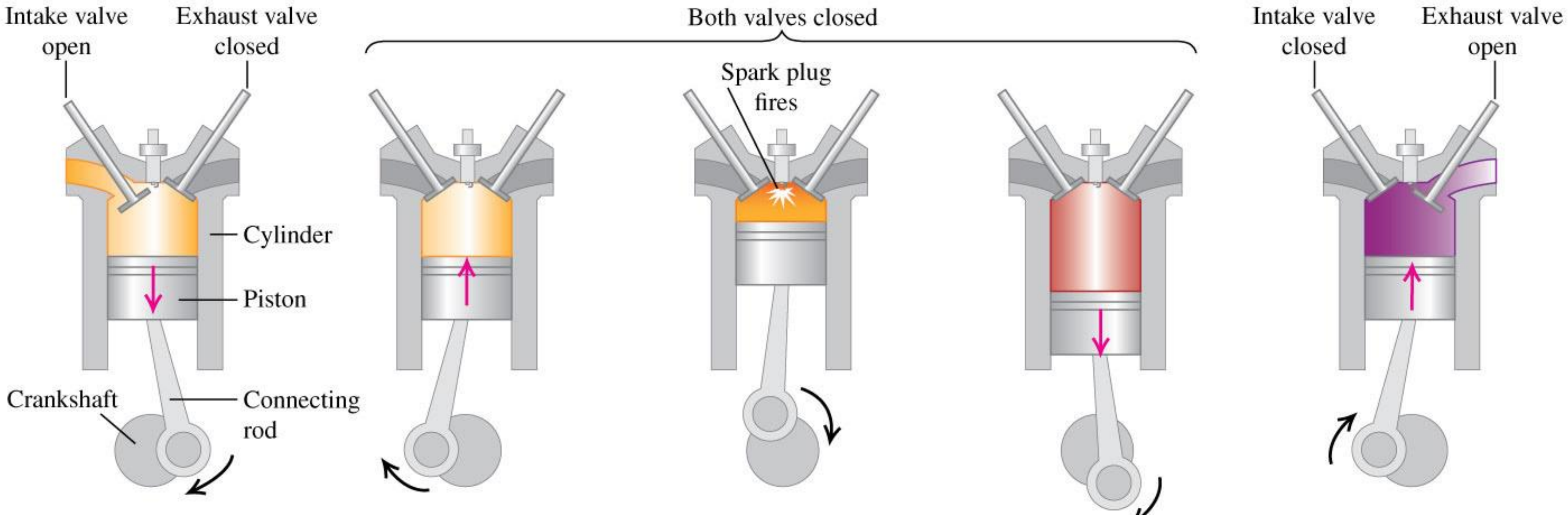
  (c) If the engine goes through 25 cycles per second, what is its power output in Watts?

  (d) How much gasoline is burned in each cycle?

  (e) How much gasoline is burned per second? Per hour?

Internal-combustion engines*

- Most cars use an internal-combustion engine (ICE) which has 5 steps during its cycle. Compression is about 8 – 10x.



① **Intake stroke:** Piston moves down, causing a partial vacuum in cylinder; gasoline–air mixture enters through intake valve.

② **Compression stroke:** Intake valve closes; mixture is compressed as piston moves up.

③ **Ignition:** Spark plug ignites mixture.

④ **Power stroke:** Hot burned mixture expands, pushing piston down.

⑤ **Exhaust stroke:** Exhaust valve opens; piston moves up, expelling exhaust and leaving cylinder ready for next intake stroke.

Refrigerators

- A **refrigerator** takes heat from a cold place (inside) and gives it off to a warmer place (the room).
  - An *input* of mechanical work is required to do this.

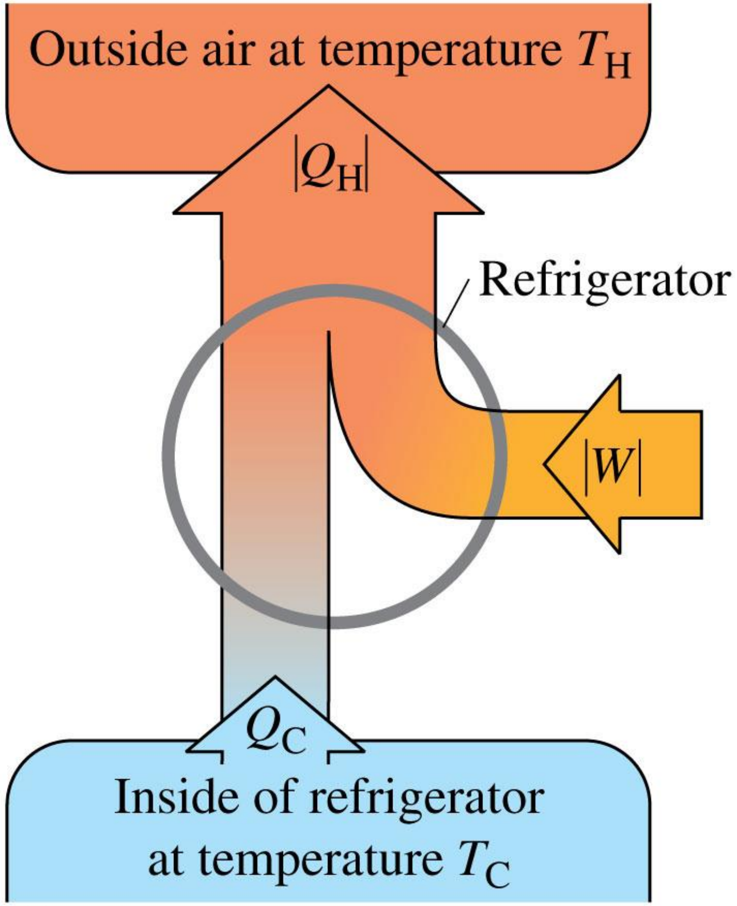
- The equation for a fridge (from 1st law) is:

$$Q_H + Q_C = W \quad \rightarrow \quad -|Q_H| + |Q_C| = -|W|$$

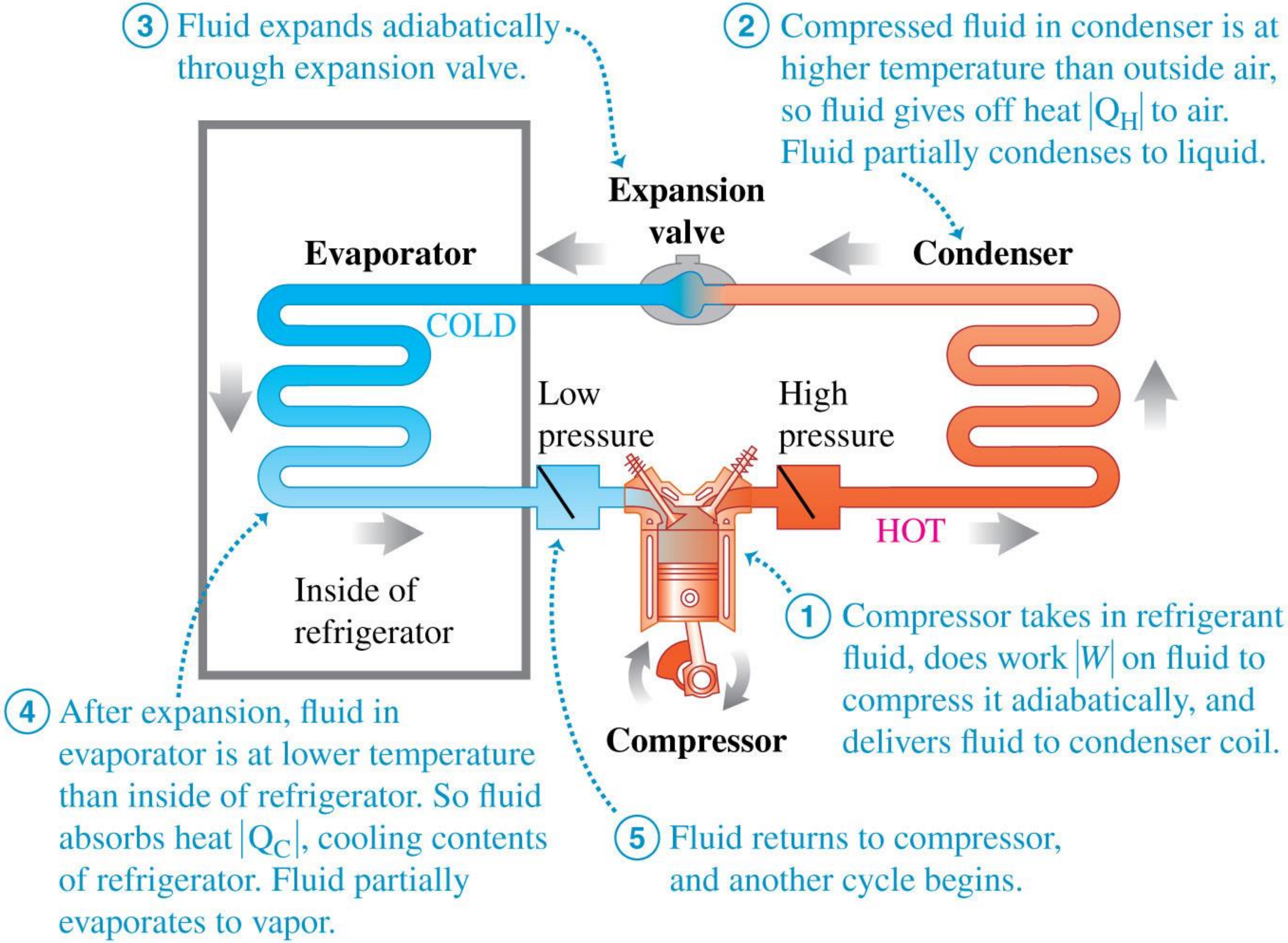
$$\boxed{|Q_H| = Q_C + |W|}$$

- The best fridge removes the greatest amount of heat (Q_C) for the least amount of work (W). The **coefficient of performance** for a fridge is:

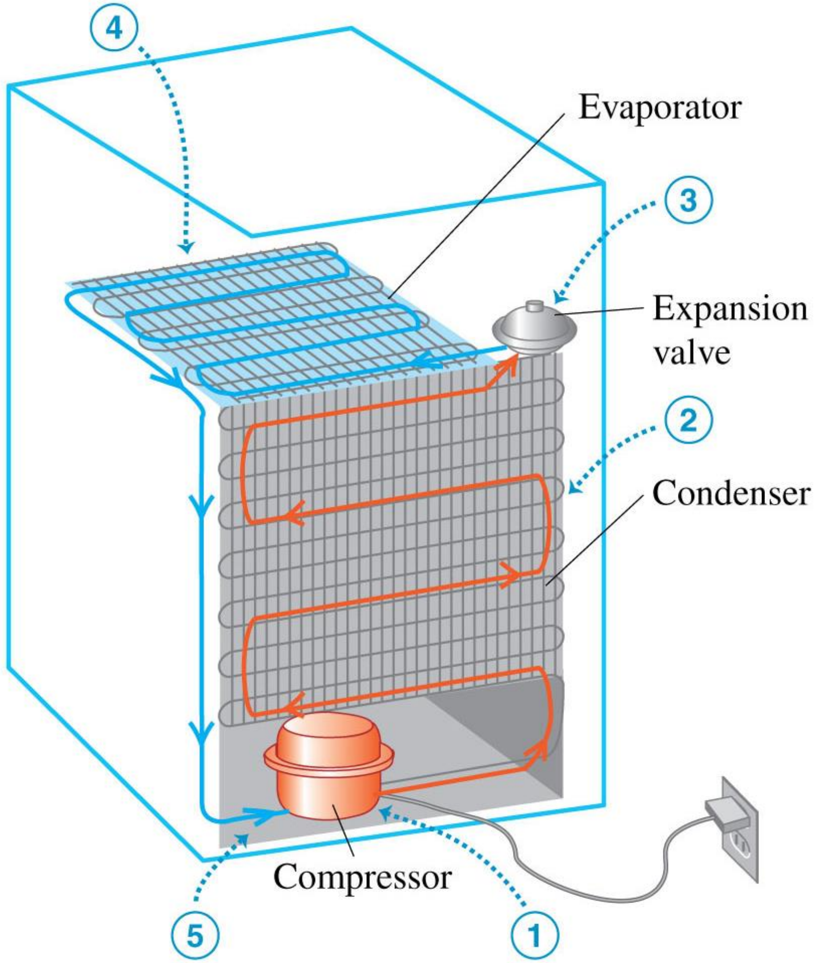
$$\boxed{K} = \frac{|Q_C|}{|W|} = \boxed{\frac{|Q_C|}{|Q_H| - |Q_C|}}$$



Principle of refrigeration cycle



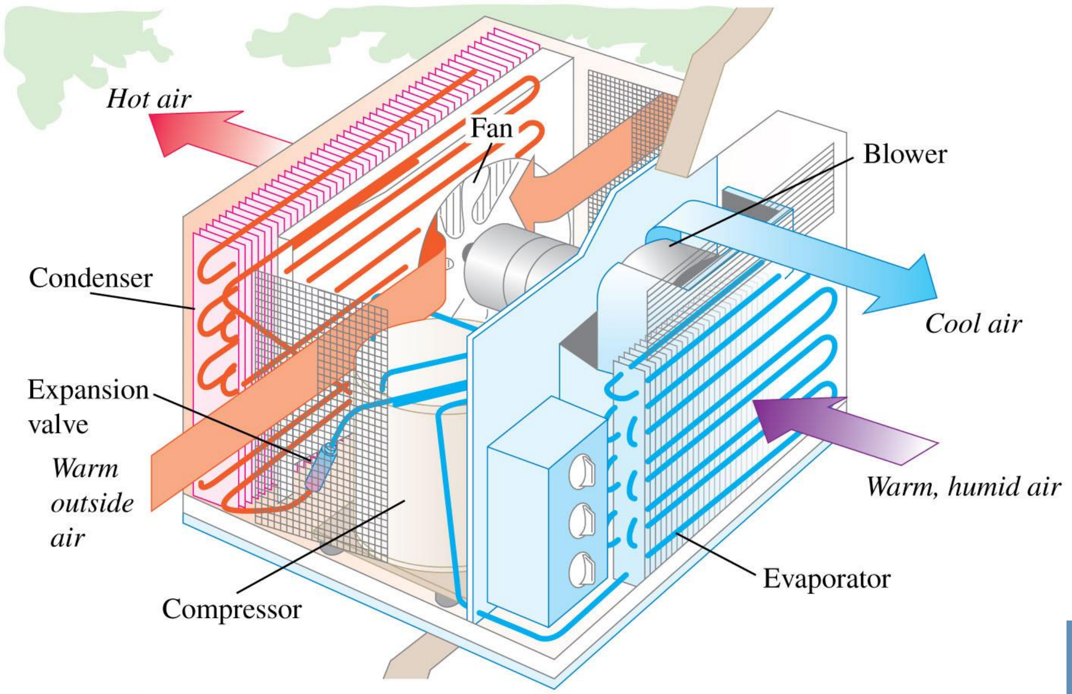
Practical refrigerators



- Both a fridge and **air conditioner** operate on the same principle.

$$\boxed{K} = \frac{|Q_C|}{|W|} = \frac{Ht}{Pt} = \boxed{\frac{H}{P}}$$

- Heat pump is the opposite.

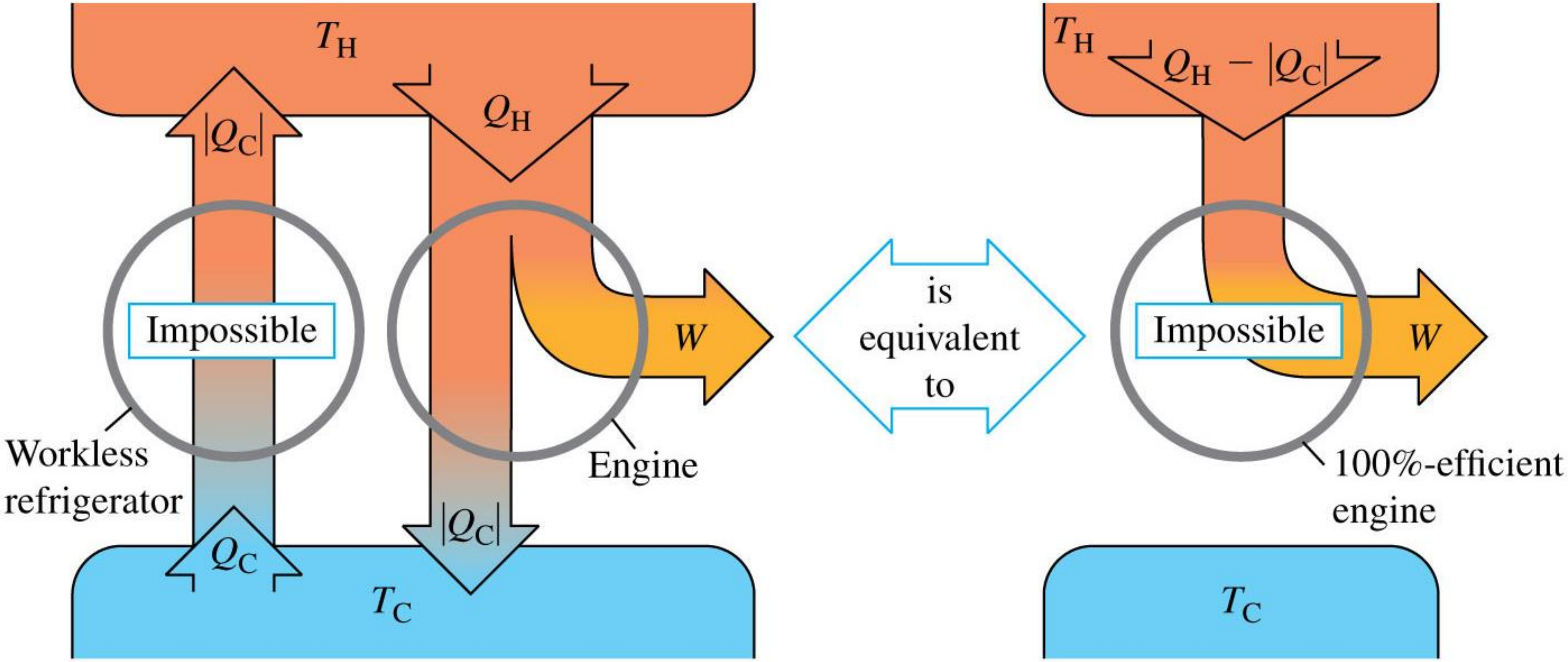


The second law of thermodynamics

- The second law can be stated in more than one way.
- Engine statement:
  It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.
- Fridge statement:
  It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.

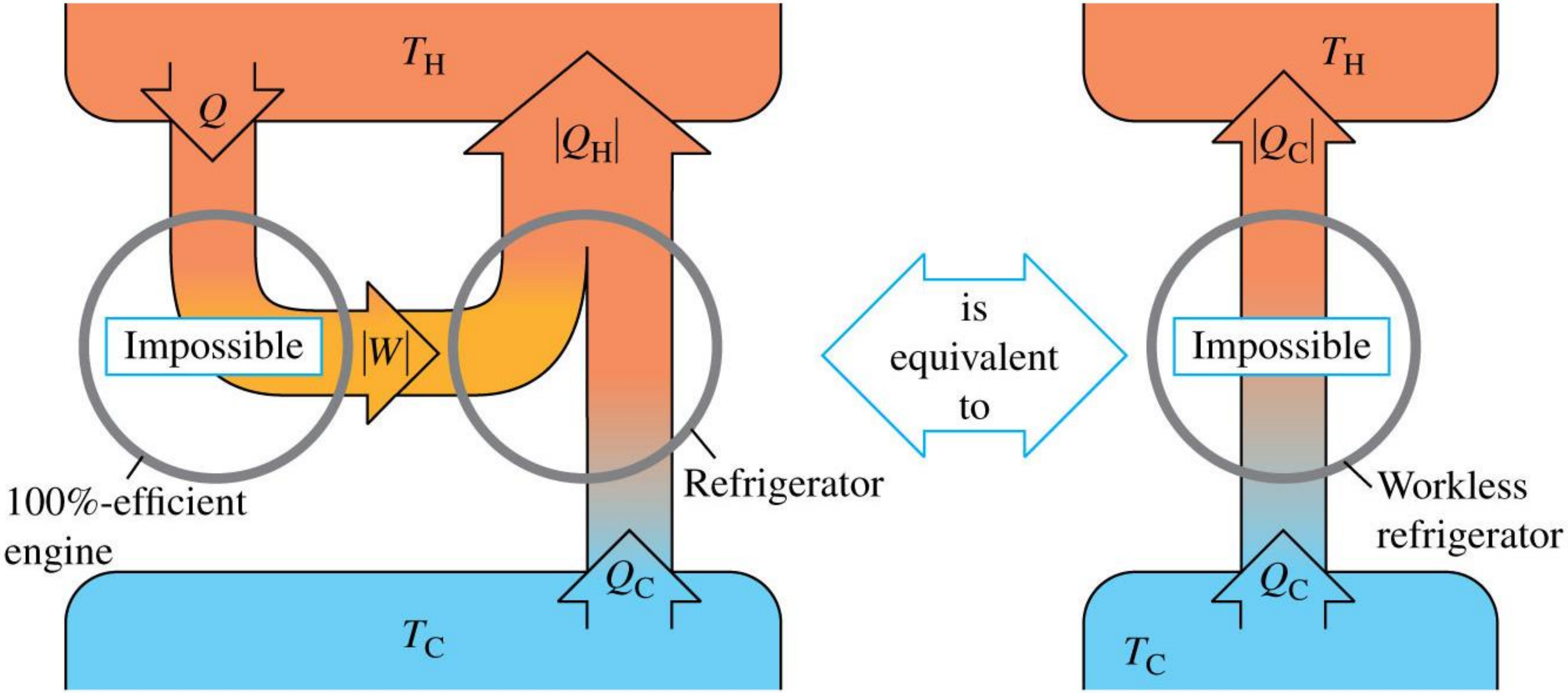
The second law of thermodynamics (workless fridge?)

- If a workless fridge was possible, it could be used in conjunction with an ordinary heat engine to form 100% efficient engine.
  - Convert the heat $(Q_H - |Q_C|)$ completely to work.



The second law of thermodynamics (100% engine?)

- If a 100% efficient engine were possible, it could be used in conjunction with an ordinary fridge to form a workless fridge, transferring heat Q_C from cold to hot reservoir with no work input.

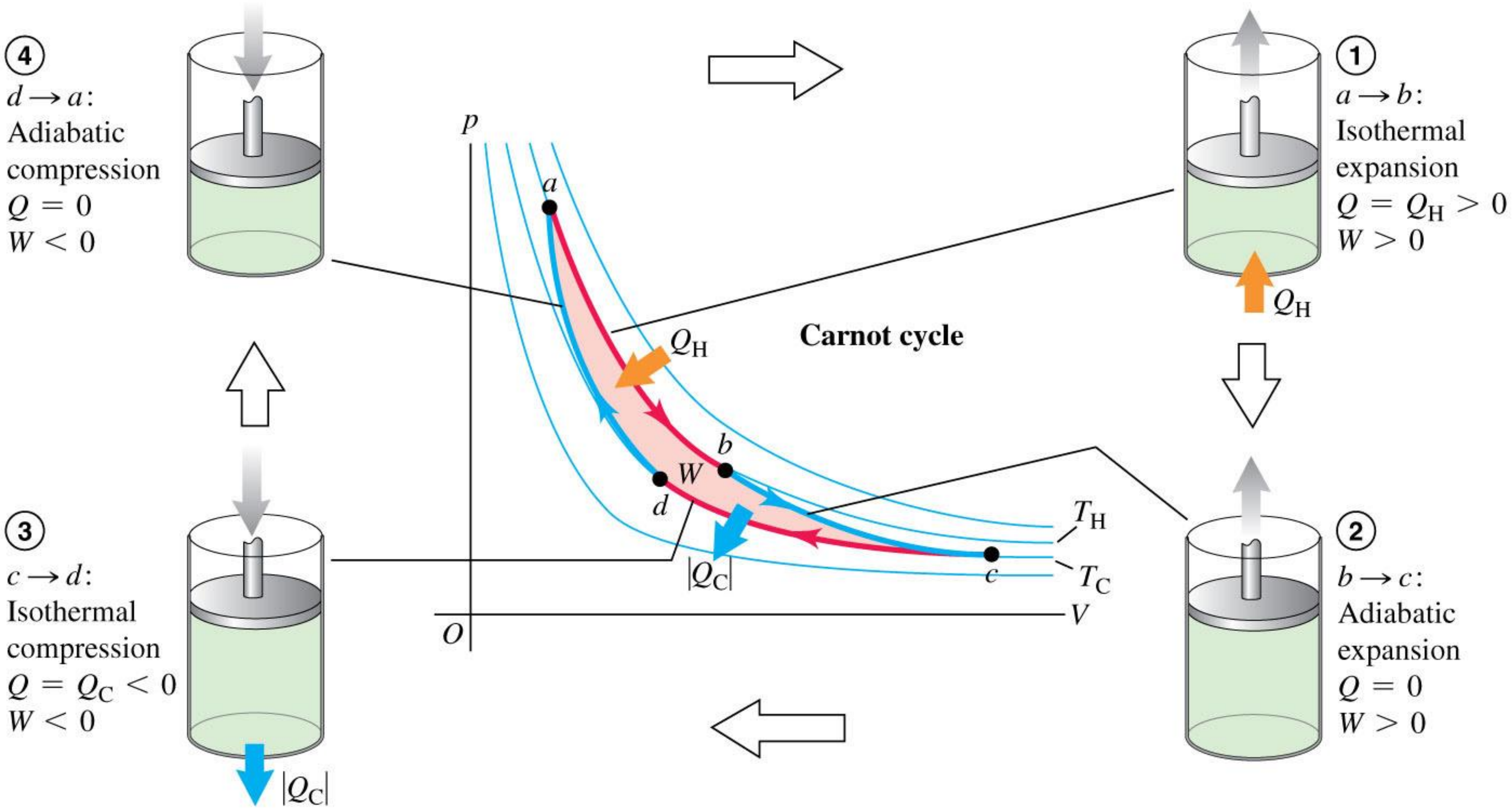


The Carnot cycle

- A **Carnot cycle** is the theoretical most efficient cycle to convert heat to work.
- Developed by studying efficiency of steam engines.
- Operates on the idea that each step in the cycle avoids *irreversible* processes.
  - During heat flow (Q_H or Q_C), both substance and reservoir at temperature T_H or T_C (isothermal).
  - During any other process where T is not T_H or T_C, there must be no heat exchanged (adiabatic).

The Carnot cycle

- A **Carnot cycle** has two adiabatic segments and two isothermal segments.



The Carnot engine and refrigerator

- The **efficiency of a Carnot engine** depends only on the temperatures of the two heat reservoirs.

$$\boxed{e_{Carnot}} = 1 - \frac{T_C}{T_H} = \boxed{\frac{T_H - T_C}{T_H}}, \qquad \text{from } \boxed{\frac{Q_C}{Q_H} = -\frac{T_C}{T_H}}$$

It is 100% efficient if $T_C = 0$ (impossible!). It is most efficient when ΔT is large. **Temperature in Kelvin!**

- The **Carnot refrigerator** is based on reversing each step in the cycle to convert the engine into a fridge. The **coefficient of performance** would be:

$$\boxed{K_{Carnot} = \frac{T_C}{T_H - T_C}}$$

Most efficient when ΔT is small.

Ex. 20.2 – Analyzing a Carnot engine

- A Carnot engine takes 2 kJ of heat from a reservoir at 500 K, does some work, and discards some heat to a reservoir at 350 K. How much work does it do, how much heat is discarded, and what is its efficiency?

Ex. 20.4 – Analyzing a Carnot Fridge

- In Ex. 20.3 (not shown), in one cycle the Carnot engine rejects $Q_C = -346\ \mathrm{J}$ of heat to the cold reservoir and does $W = 230\ \mathrm{J}$ of work. What is the coefficient of performance if this engine is run in reverse as a fridge between the temperatures $227℃$ and $27℃$?

Entropy and disorder

- Basically any process in nature proceeds towards *increasing* randomness and disorder.

- **Eg**. Adding heat to a body gives more average molecular speed and motion of molecules becomes more random.
  Eg2. Exploding a firecracker: ordered chemicals disperse in all direction and random kinetic energy of all fragments increases.

- **Entropy** is a quantitative description of randomness.

Entropy in a reversible process

- We introduce symbol S for **entropy**.

- Consider a *tiny* isothermal expansion of an **ideal gas**. The *tiny* amount of heat added causes a *tiny* change in volume.
  - No change in T and therefore no change in U.
  - All the heat goes into the work done on the gas:

$$\boxed{dQ} = dW = p\,dV = \boxed{\frac{nRT}{V}dV}$$

$$\frac{dV}{V} = \frac{dQ}{nRT}$$

$$dS = \frac{dQ}{T} \quad \rightarrow \quad \boxed{\Delta S} = S_2 - S_1 = \boxed{\frac{Q}{T}}$$

For a **reversible isothermal process**.

Entropy in a reversible process

- We can generalize our entropy definition equation $\Delta S = Q/T$ to any reversible process.

  At every step, there's a *tiny* quantity of heat dQ added to the system at temperature T to increase entropy. We integrate dQ/T over all the added heat:

$$\boxed{\Delta S = \int_1^2 \frac{dQ}{T}}$$

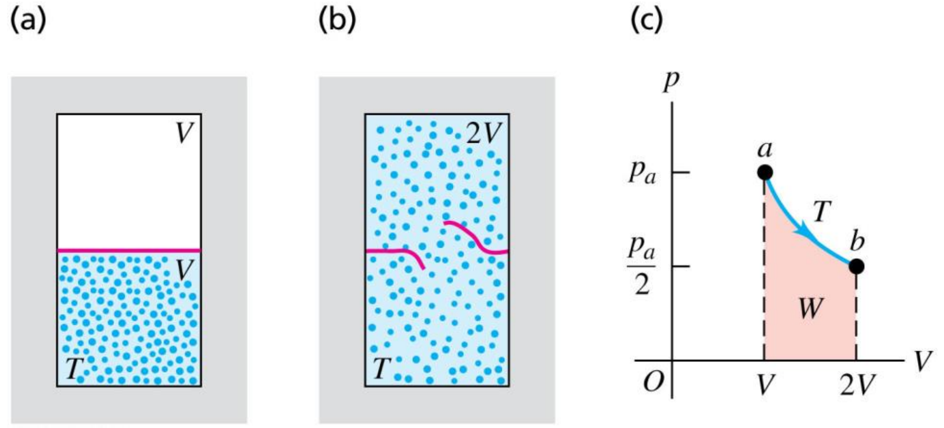
- Since entropy is a measure of randomness of a system, it does not depend on the path to get from one state to the next, only on the current state.
  - The change from state 1 to 2 (ΔS) is the same for any and all paths.

Ex. 20.6 – Entropy change for ΔT

- One kg of water at $0°\text{C}$ is heated to $100°\text{C}$. Compute the change in entropy. Assume the specific heat of water is constant at $4190\ \text{J/kg} \cdot \text{K}$ over this temperature range.

Ex. 20.8 – Entropy change in free expansion

- A partition divides a thermally insulated box into two parts, each of volume V. Initially, one compartment contains n moles of ideal gas at temperature T and the other is evacuated. We break the partition and the gas expands. What is the entropy change in this free-expansion process?



Entropy and the second law

- We can restate the second law in terms of entropy now:

  No process is possible in which the total entropy decreases, when all systems taking part in the process are included.

- Entropy always increases or remains constant (only for reversible processes) when all processes are included.

- This is why heat can't spontaneously flow from cold object to hot object (**fridge** statement).

- You can't create a heat engine which extracts heat and converts it all to work and the system remains in the same state (**engine** statement).

Entropy and the second law

- Two examples of entropy increase:

- 1) Mixing of hot and cold water doesn't lose energy but loses the opportunity to convert heat to work. (look at textbook **Ex. 20.10** if interested)
  - Hot and cold water will never un-mix.

- 2) Mixing of coloured ink and water goes through stages but eventually the spread will be random.
  - No spontaneous un-mixing. It would mean a decrease in entropy.

- Plausible consequence is **HEAT DEATH.**