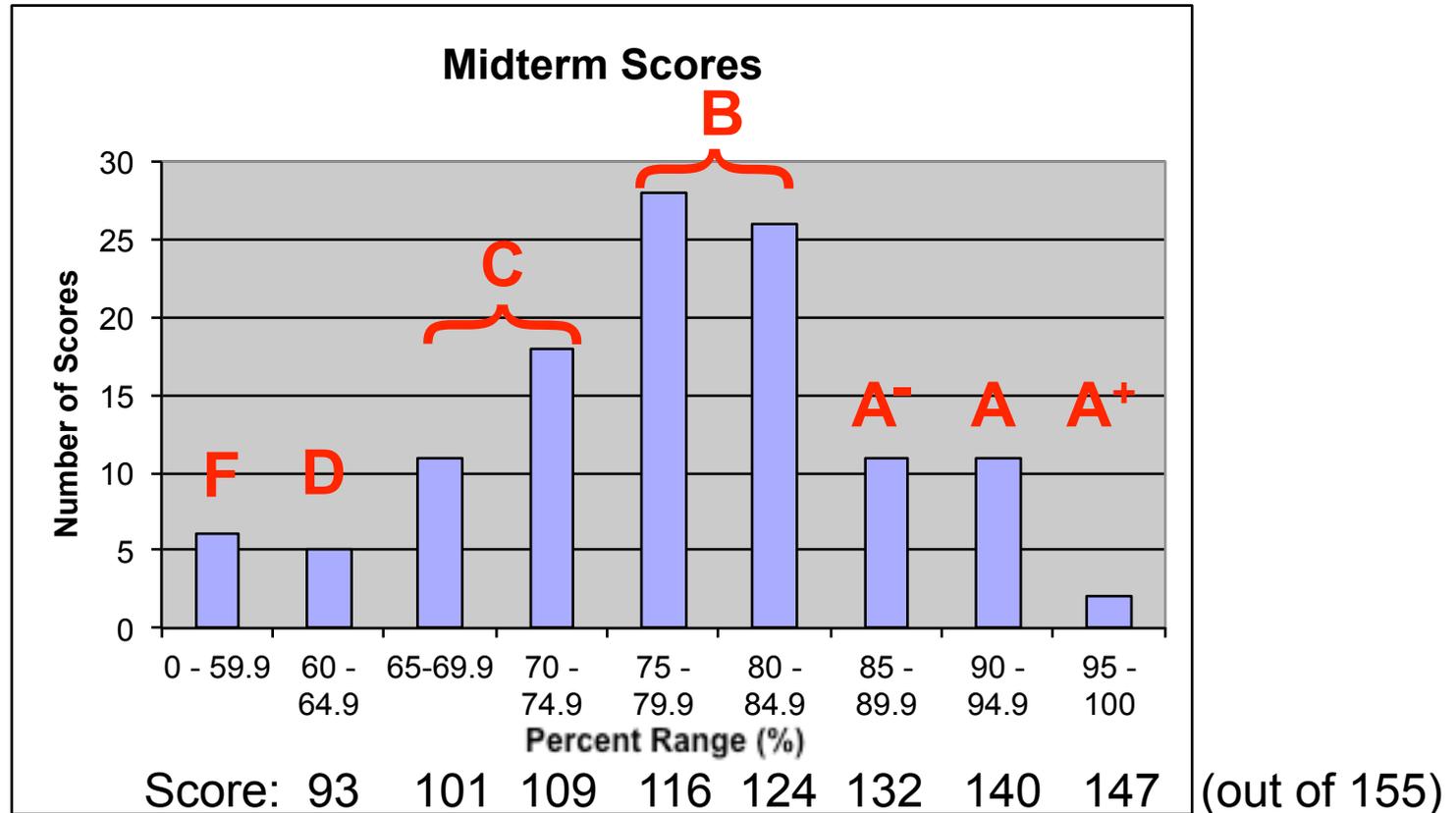


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The two problems with the fewest correct answers were #10 and #24.

10. What would be the greatest effect on the ideal gas law if there is a slight attractive force between the molecules?

A) At low densities, the pressure would be less than that predicted by the ideal gas law.

This is why the first factor in the van der Waals equation is $(P + a/v^2)$

18-5 Van der Waals Equation of State

We assume that some fraction b of the volume per mole is unavailable due to the finite size of the molecules. We also expect that the **pressure will be reduced by a factor proportional to the square of the density, due to interactions between the molecules.** This gives the Van der Waals equation of state; the constants a and b are found experimentally for each gas:

$$\left(P + \frac{a}{(V/n)^2} \right) \left(\frac{V}{n} - b \right) = RT.$$

From Lecture 2

Problem 24 was one that I discussed in Lecture 5:

An athlete is sitting unclothed in a locker room whose dark walls are at a temperature of 15°C . Calculate his net rate of heat loss by radiation, assuming a skin temperature of 34°C and $\epsilon = 0.70$. Take the surface area of the body not in contact with the chair to be 1.5 m^2 .

Answer: Let $T_1 = 34^{\circ}\text{C} = 307\text{K}$, $T_2 = 15^{\circ}\text{C} = 288\text{K}$

$$\frac{\Delta Q}{\Delta t} = \epsilon \sigma A (T_1^4 - T_2^4), \text{ where } \sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4.$$

$$= (0.70)(5.67 \times 10^{-8} \text{ W/m}^2 \text{K}^4)(1.5 \text{ m}^2) (T_1^4 - T_2^4)$$

$$= 120 \text{ W}$$

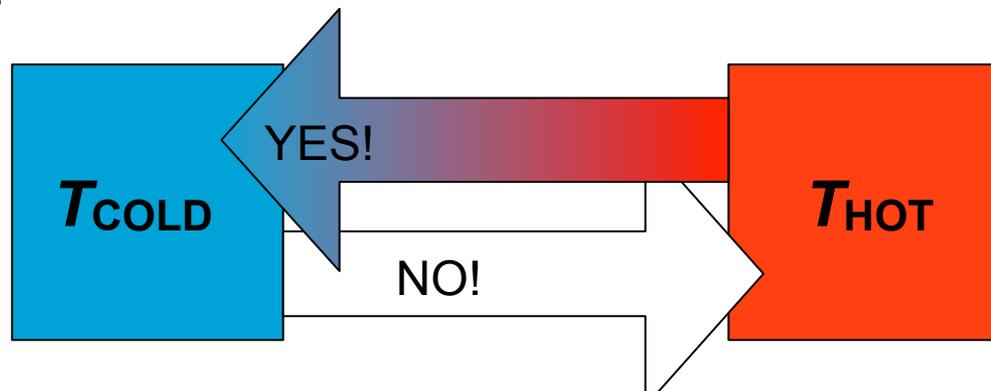
You have to include the radiation from the walls!

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The 2nd Law of Thermodynamics

The second law of thermodynamics is a statement about which processes occur and which do not. This is the Clausius statement of the second law:

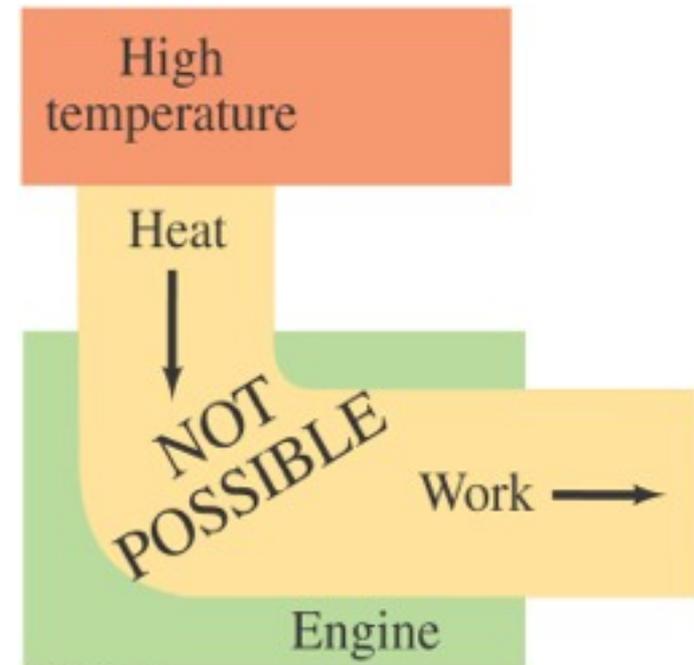
Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.



20-2 Heat Engines

No heat engine can have an efficiency of 100%. This is the Kelvin-Planck statement of the second law of thermodynamics:

No device is possible whose sole effect is to transform a given amount of heat completely into work.

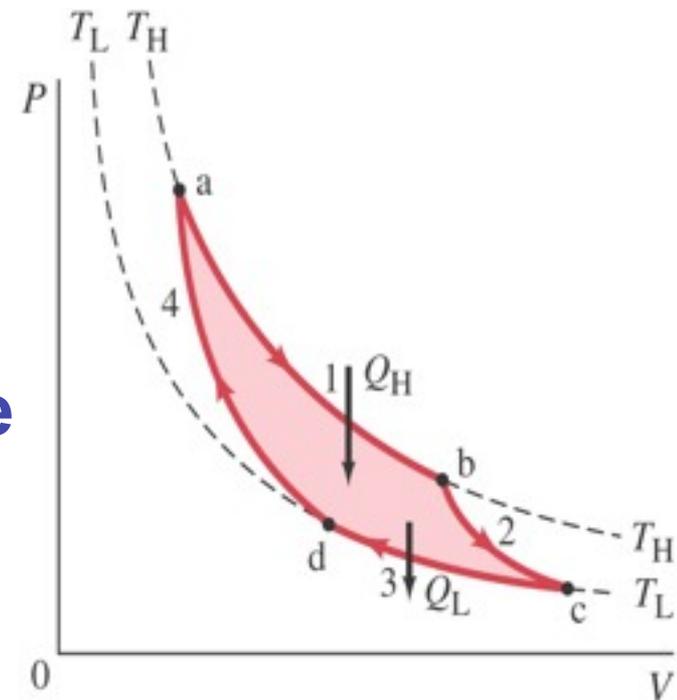


Today's lecture will introduce a third statement of the second law, in terms of entropy.

20-3 Reversible Processes

Classical thermodynamics only considers systems in equilibrium states. The **equilibrium state** of an ideal gas can be specified by giving T , V , and P ; then $PV/RT=n$.

A **reversible process** is one carried out so slowly that every intermediate state is in equilibrium. (Any process carried out rapidly will cause nonuniformities of temperature and pressure within the gas, so we cannot know the exact path in a P - V diagram.)

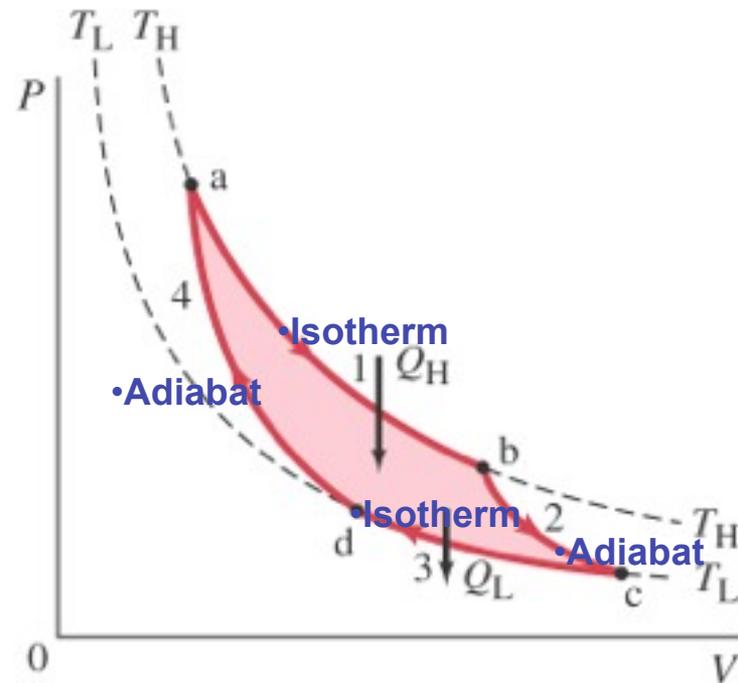


20-3 Reversible and Irreversible Processes; the Carnot Cycle

The **Carnot cycle** allows us to calculate the maximum possible efficiency of a heat engine. Each leg of the cycle is reversible.

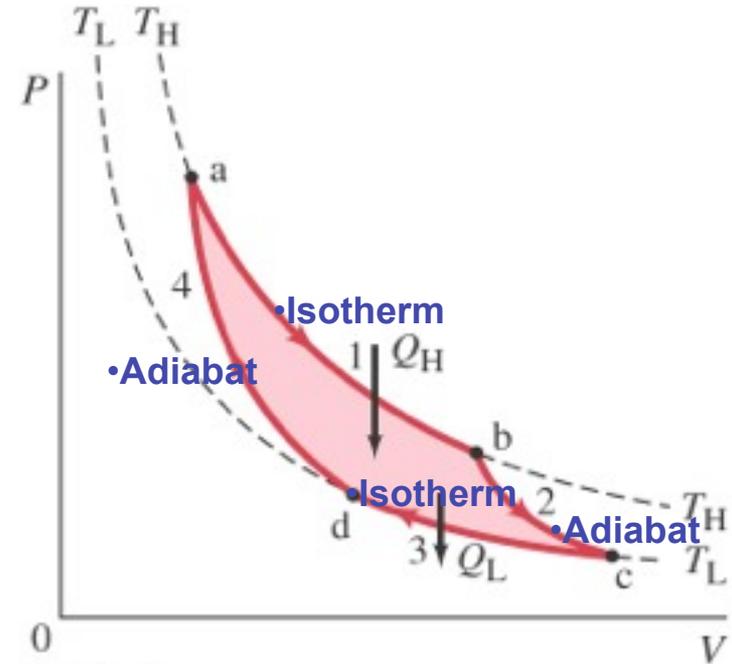
The Carnot cycle consists of:

- Isothermal expansion ab
- Adiabatic expansion bc
- Isothermal compression cd
- Adiabatic compression da



The Carnot cycle consists of:

- Isothermal expansion ab
- Adiabatic expansion bc
- Isothermal compression cd
- Adiabatic compression da



We will show that for an ideal gas Carnot cycle

the efficiency

$$e = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

because for a Carnot cycle

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

Proof that for a Carnot cycle

with an ideal gas $\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$.

In the isothermal processes

$$Q_H = W_{ab} = nRT_H \ln \frac{V_b}{V_a}$$

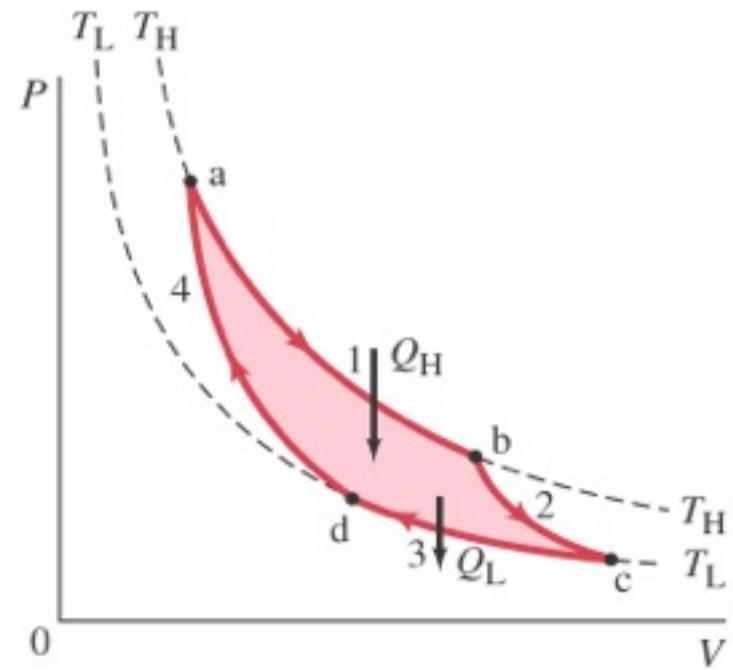
and $Q_L = nRT_L \ln \frac{V_c}{V_d}$. For the

adiabatic processes $P_b V_b^\gamma = P_c V_c^\gamma$ and $P_d V_d^\gamma = P_a V_a^\gamma$,

and for an ideal gas $\frac{P_b V_b}{T_H} = \frac{P_c V_c}{T_L}$ and $\frac{P_d V_d}{T_L} = \frac{P_a V_a}{T_H}$.

Dividing, $T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1}$ and $T_L V_d^{\gamma-1} = T_H V_a^{\gamma-1}$.

Dividing these eqns, $\left(\frac{V_b}{V_a}\right)^{\gamma-1} = \left(\frac{V_c}{V_d}\right)^{\gamma-1}$ or $\frac{V_b}{V_a} = \frac{V_c}{V_d}$.



Proof that for a Carnot cycle

with an ideal gas $\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$.

In the isothermal processes

$$Q_H = W_{ab} = nRT_H \ln \frac{V_b}{V_a}$$

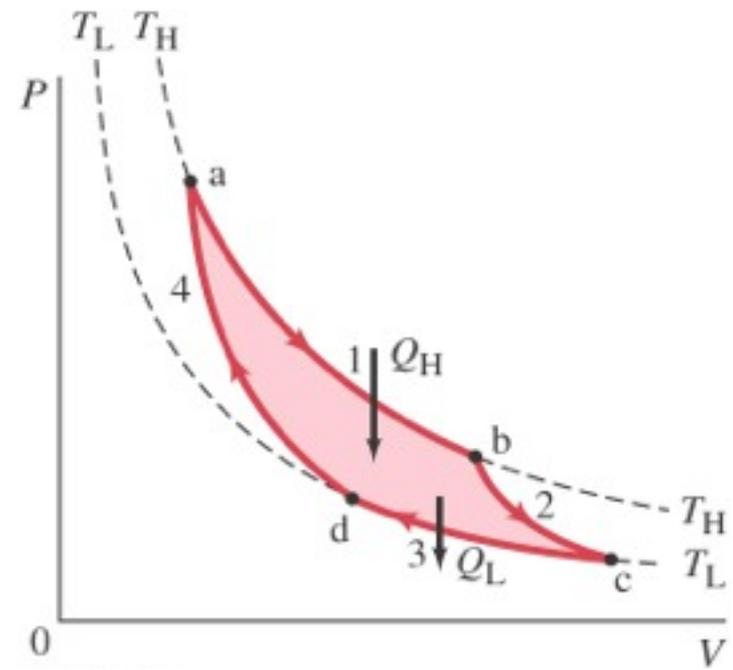
and $Q_L = nRT_L \ln \frac{V_c}{V_d}$.

We just found that $\frac{V_b}{V_a} = \frac{V_c}{V_d}$.

Substituting into the expressions above for Q_H , Q_L

we see that $\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$. Thus for a Carnot cycle,

the efficiency $e = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$



We see that for an ideal reversible Carnot cycle, the efficiency can be written in terms of the temperatures:

$$e_{\text{ideal}} = 1 - \frac{T_L}{T_H}.$$

From this we see that 100% efficiency can be achieved only if the cold reservoir is at absolute zero, which is impossible. Thus we derive the Kelvin-Planck statement of the 2nd Law:

No device is possible whose sole effect is to transform a given amount of heat completely into work.

Real engines have some frictional losses; the best achieve 60–80% of the Carnot value of efficiency.

20-3 Reversible and Irreversible Processes; the Carnot Engine

Example 20-2: A phony claim?

An engine manufacturer makes the following claims: An engine's heat input per second is 9.0 kJ at 435 K. The heat output per second is 4.0 kJ at 285 K. Can you believe these claims?

20-3 Reversible and Irreversible Processes; the Carnot Engine

Example 20-2: A phony claim?

An engine manufacturer makes the following claims: An engine's heat input per second is 9.0 kJ at 435 K. The heat output per second is 4.0 kJ at 285 K. Can you believe these claims?

Answer: The claims imply an efficiency of

$$e = 1 - \frac{Q_L}{Q_H} = 1 - \frac{4.0 \text{ kJ}}{9.0 \text{ kJ}} = 0.56,$$

This is greater than the maximum possible e

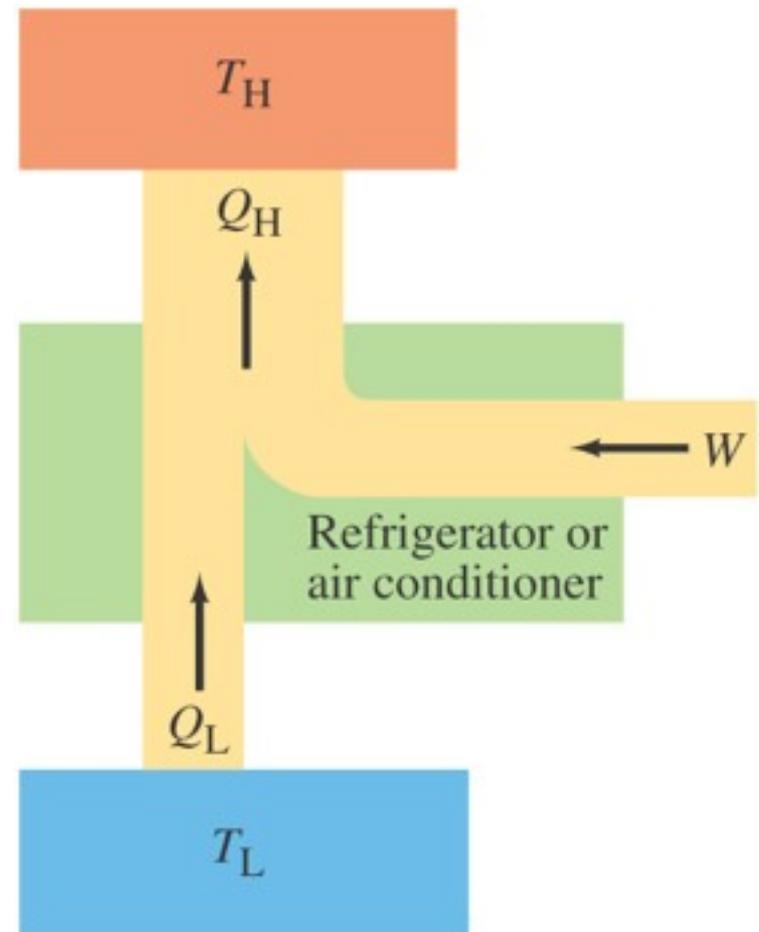
$$e_{\text{ideal}} = 1 - \frac{T_L}{T_H} = 1 - \frac{285 \text{ K}}{435 \text{ K}} = 0.34,$$

so the claim is not credible.

20-4 Refrigerators, Air Conditioners, and Heat Pumps

These appliances are essentially heat engines operating in reverse.

By doing work, heat is extracted from the cold reservoir and exhausted to the hot reservoir.



20-4 Refrigerators, Air Conditioners, and Heat Pumps

Refrigerator performance is measured by the coefficient of performance (COP):

$$\text{COP} = \frac{Q_L}{W}$$


What we want

What we pay for

Substituting:

$$\text{COP} = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

For an ideal Carnot refrigerator $Q_H/Q_L = T_H/T_L$,
so

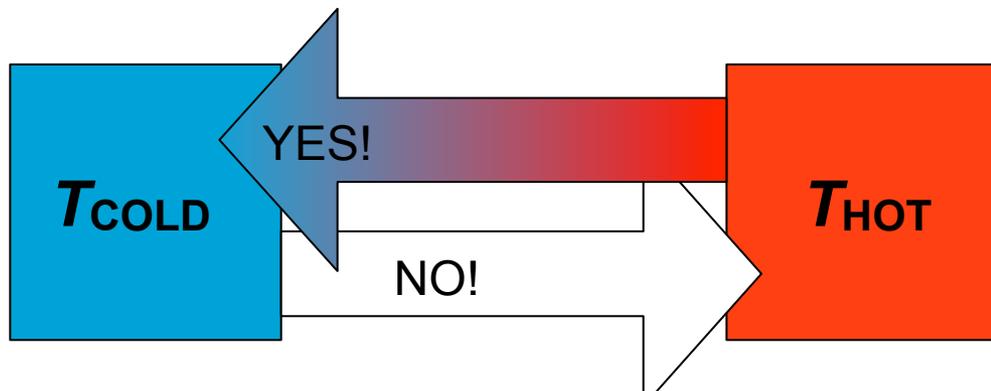
$$\text{COP}_{\text{ideal}} = \frac{T_L}{T_H - T_L}$$

For an ideal refrigerator,

$$\text{COP}_{\text{ideal}} = \frac{T_L}{T_H - T_L} = \frac{Q_L}{W}.$$

Since $T_H - T_L > 0$, a perfect refrigerator ($W = 0$) is impossible. This is the Clausius statement of the 2nd Law, mentioned earlier:

Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.



20-4 Refrigerators, Air Conditioners, and Heat Pumps

Example 20-4: Making ice.

A freezer has a COP of 3.8 and uses 200 W of power. How long would it take this otherwise empty freezer to freeze an ice-cube tray that contains 600 g of water at 0°C? ($L = 333 \text{ kJ/kg}$)

20-4 Refrigerators, Air Conditioners, and Heat Pumps

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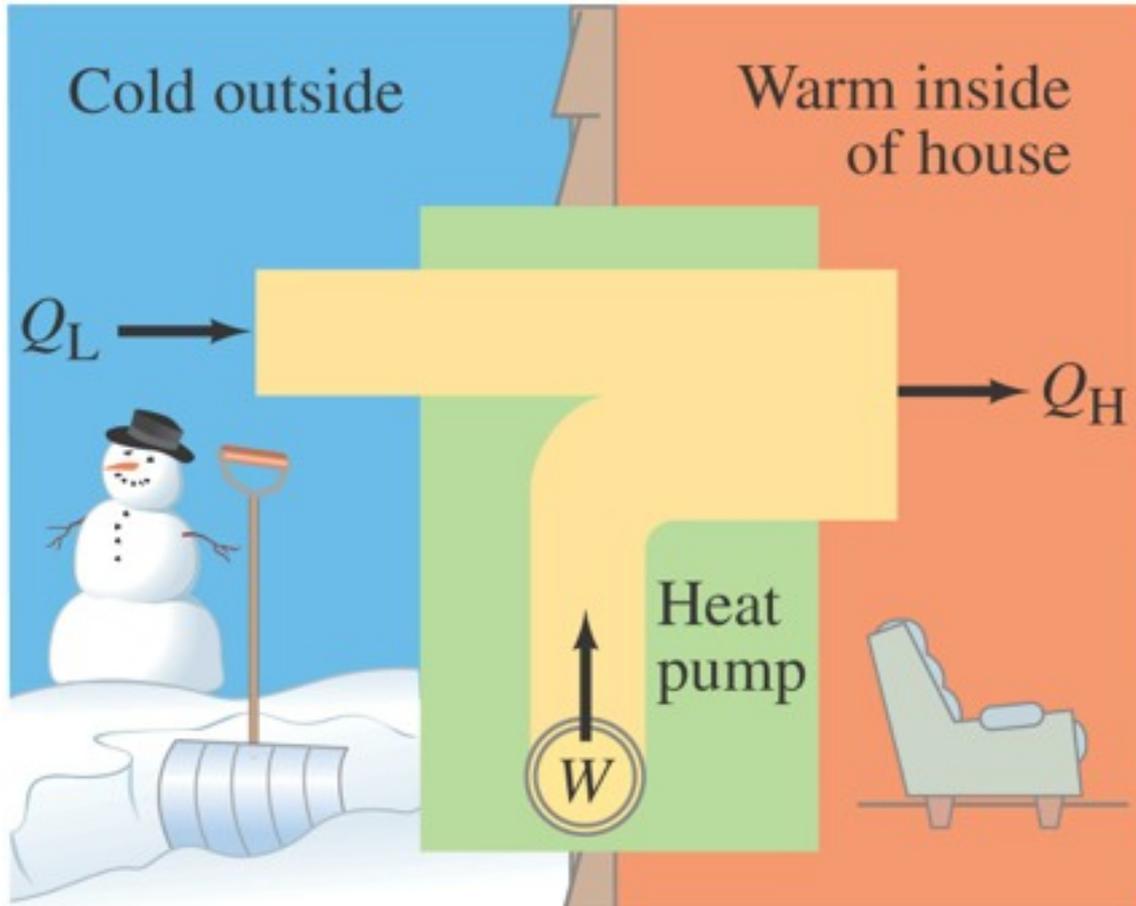
Answer: $\text{COP} = Q_L/W = 3.8$, so

$$Q_L/s = 3.8 \text{ W/s} = 3.8 (200 \text{ W}) = 760 \text{ W} = 0.76 \text{ kJ/s}$$

The latent heat of the ice-water phase transition is $L = 333 \text{ kJ/kg}$, so for 0.6 kg the needed $Q_L = 0.6 (333 \text{ kJ}) = 200 \text{ kJ}$. The time required is $t = 200 \text{ kJ}/0.76 \text{ kJ/s} = 260 \text{ s} = 4.4 \text{ minutes}$.

20-4 Refrigerators, Air Conditioners, and Heat Pumps

A heat pump can heat a house in the winter:



The heat pump coefficient of performance is defined as

$$\text{COP} = \frac{Q_H}{W}.$$

As usual, it's what we want divided by what we pay for.

Example 20-5: Heat pump.

A heat pump has a coefficient of performance of 3.0 and is rated to do work at 1500 W.

(a) How much heat can it add to a room per second?

(b) If the heat pump were turned around to act as an air conditioner in the summer, what would you expect its coefficient of performance to be, assuming all else stays the same?

Example 20-5: Heat pump.

A heat pump has a coefficient of performance of 3.0 and its power requirement is 1500 W.

(a) How much heat can it add to a room per second? **Answer:** $Q_H/s = (\text{COP})W/s = 4500 \text{ W}$.

(b) If the heat pump were turned around to act as an air conditioner in the summer, what would you expect its coefficient of performance to be, assuming all else stays the same?

Answer: Its refrigerator $\text{COP} = Q_L/W$ where $Q_L = Q_H - W = 3000 \text{ J/s}$. Thus its air conditioning $\text{COP} = 3000/1500 = 2.0$.

20-5 Entropy

Definition of the change in entropy S when an amount of heat Q is added:

$$\Delta S = \frac{Q}{T}$$

if the process is reversible and the temperature is constant. Otherwise,

$$dS = \frac{dQ}{T}.$$



“I propose to name the quantity S the entropy of the system, after the Greek word [τροπή *tropē*], the transformation. I have deliberately chosen the word entropy to be as similar as possible to the word energy: the two quantities to be named by these words are so closely related in physical significance that a certain similarity in their names appears to be appropriate.” Clausius probably chose “ S ” in honor of [Sadi Carnot](#), whose 1824 paper had inspired Clausius.



Sadi Carnot

Rudolf Clausius

Which has higher entropy – a kilogram of ice at 0 °C or a kilogram of water at 0 °C?

A. Ice

B. Water

C. No difference

Which has higher entropy – a kilogram of ice at 0 °C or a kilogram of water at 0 °C?

A. Ice

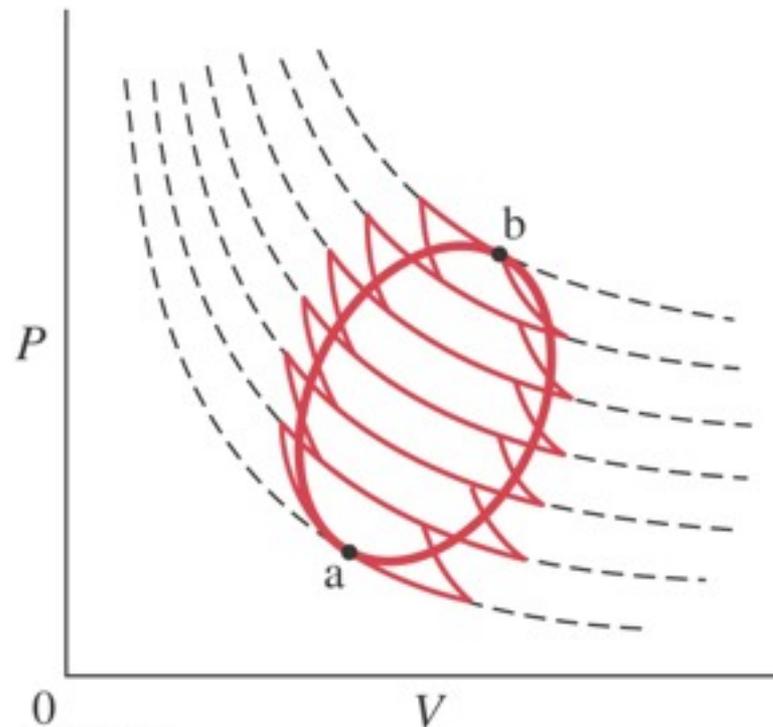
B. Water

**1 kg of water has $\Delta S = L_{fusion}/T$
 $= 333 \text{ kJ} / 273\text{K} = 1.22 \text{ kJ/K}$
higher entropy than a kg of ice**

C. No difference

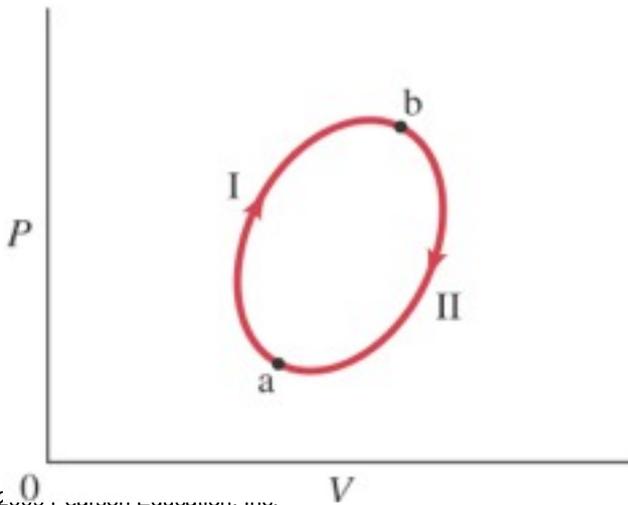
20-5 Entropy

Any reversible cycle can be written as a succession of Carnot cycles; therefore, what is true for a Carnot cycle is true of all reversible cycles.



20-5 Entropy

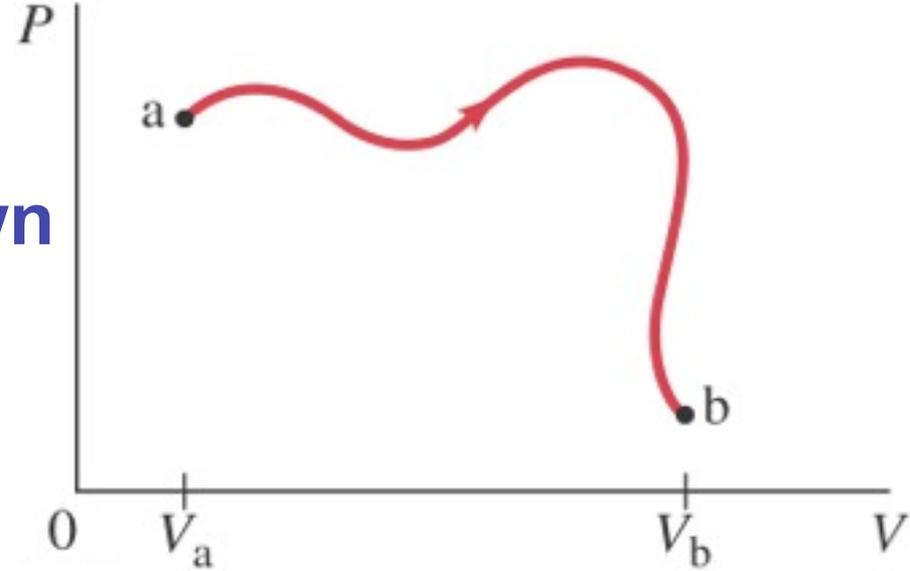
Since for any Carnot cycle $Q_H/Q_L = T_H/T_L$ so $Q_H/T_H - Q_L/T_L = 0$. Thus, if we approximate any reversible cycle as an infinite sum of Carnot cycles, we see that the integral of dQ/T around any closed path is zero. This means that **entropy is a state variable**, like internal energy. The change in its value depends only on the initial and final states.



(Note the analogy with the path integral argument that shows the potential energy change depends only on the initial and final states, not the path.)

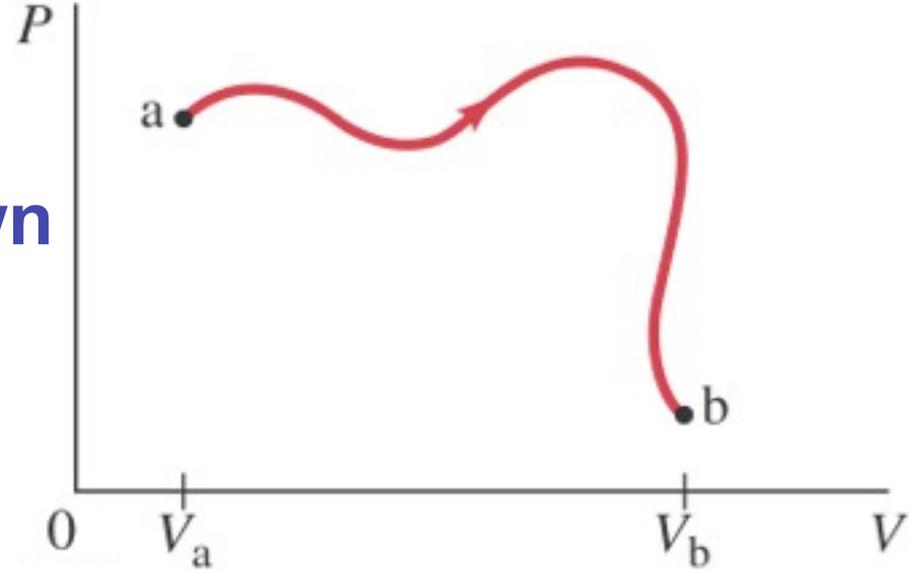
Change of Entropy

An ideal gas of n moles undergoes the reversible process from a to b shown at right, where $T_a = T_b$. Calculate the change of entropy.



Change of Entropy

An ideal gas of n moles undergoes the reversible process from a to b shown at right, where $T_a = T_b$. Calculate the change of entropy $\Delta S = S_b - S_a$.

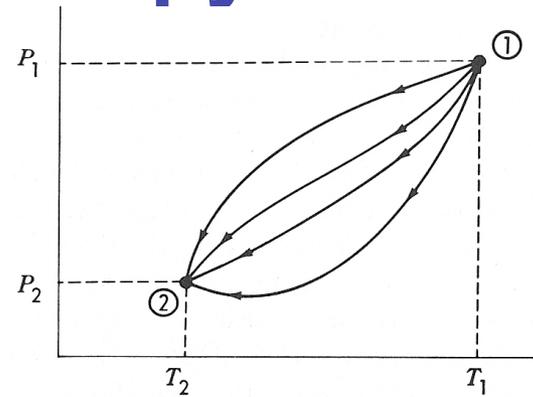
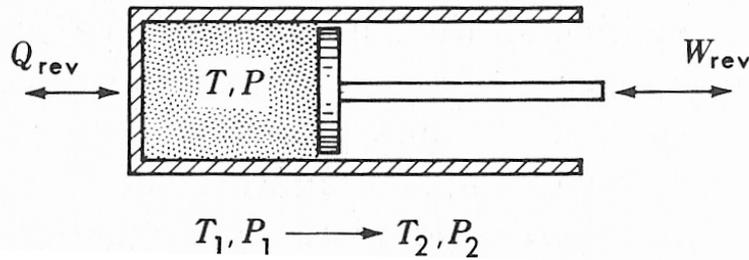


Answer: Entropy is a state variable, so ΔS is the same for any path. Since $T_a = T_b$ consider an isothermal process connecting a and b, so that

$$Q = W = nRT \ln(V_b/V_a).$$

$$\text{Then } \Delta S = Q/T = W/T = nR \ln(V_b/V_a).$$

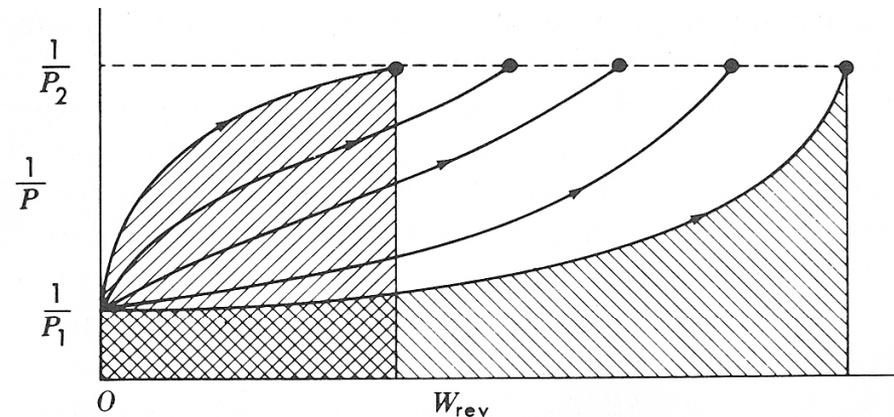
Analogy between Entropy and Volume



Suppose that we follow various reversible paths in a P - T diagram. We plot T vs. P , T vs. V , etc., and look for an invariant. We plot $1/P$ vs. W_{rev} and find that the area under the curves

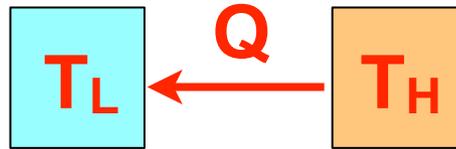
$$\int \frac{1}{P} dW_{\text{rev}} = \Delta V$$

is always the same!
In differential form this



is $\frac{dW_{\text{rev}}}{P} = dV$ or $dW_{\text{rev}} = P dV$ as we already knew. Entropy is like this, but hard to visualize.

20-6 Entropy and the Second Law of Thermodynamics



$$\Delta S = Q/T_L - Q/T_H > 0$$

The total entropy always increases when heat flows from a warmer object to a colder one in an isolated two-body system. The heat transferred is the same, and the cooler object is at a lower average temperature than the warmer one, so the entropy gained by the cooler one is always more than the entropy lost by the warmer one.

20-6 Entropy and the Second Law of Thermodynamics

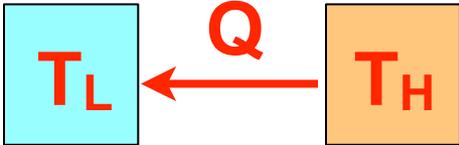
The fact that after every interaction the entropy of the system plus the environment never decreases is another way of putting the 2nd Law:

The entropy of an isolated system never decreases. It either stays constant (reversible processes) or increases (irreversible processes).

20-6 Entropy and the Second Law of Thermodynamics

The fact that after every interaction the entropy of the system plus the environment never decreases is another way of putting the 2nd Law:

The entropy of an isolated system never decreases. It either stays constant (reversible processes) or increases (irreversible processes).

$\Delta S = Q/T_L - Q/T_H > 0$ for  shows that

Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object. (Clausius 2nd Law)

20-6 Entropy and the Second Law of Thermodynamics

Example 20-D: Heat transfer.

Suppose that 1 kg of ice is in contact with a heat reservoir infinitesimally warmer than 0°C. Given that $L_{\text{ice-water}} = 333 \text{ kJ/kg}$, calculate

a. ΔS_{ice}

b. $\Delta S_{\text{heat reservoir}}$

c. ΔS_{total}

20-6 Entropy and the Second Law of Thermodynamics

Example 20-D: Heat transfer.

Suppose that 1 kg of ice is in contact with a heat reservoir infinitesimally warmer than 0°C. Given that $L_{\text{ice-water}} = 333 \text{ kJ/kg}$, calculate

a. $\Delta S_{\text{ice}} = + 333 \text{ kJ} / 273 \text{ K} = 1.22 \text{ kJ/K}$

b. $\Delta S_{\text{heat reservoir}}$

c. ΔS_{total}

20-6 Entropy and the Second Law of Thermodynamics

Exercise 20-D: Heat transfer.

Suppose that 1 kg of ice is in contact with a heat reservoir infinitesimally warmer than 0°C. Given that $L_{\text{ice-water}} = 333 \text{ kJ/kg}$, calculate

a. $\Delta S_{\text{ice}} = + 333 \text{ kJ} / 273 \text{ K} = 1.22 \text{ kJ/K}$

b. $\Delta S_{\text{heat reservoir}} = -1.22 \text{ kJ/K}$

c. $\Delta S_{\text{total}} = 0$

This is a good example of a reversible transformation.