

- Motivation for the Second Law
- Heat Engines and the Second Law
- The Carnot Engine and its Efficiency
- Absolute Zero
- Refrigerators and the Second Law

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Chapter 15, Part A

Motivation for the Second Law

- Conservation laws forbid certain things.
  - Conservation of electric charge
  - Conservation of momentum
  - Conservation of angular momentum
  - Conservation of energy
- However, we can also describe various hypothetical processes that are consistent with all known conservation laws, and yet have never been observed.

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### Heat Engines and the Second Law: I

- It is possible (even easy) to "turn work completely into heat."
- The function of a heat engine is the reverse: to employ heat to perform useful work.
- The efficiency  $\varepsilon$  of a cyclic heat engine is defined as the ratio of work done to hightemperature heat invested:

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Heat Engines and the Second Law: II

• One version of the Second Law of <u>Thermodynamics</u> states that:

"It is impossible to construct a perfect heat engine."

- This means that the efficiency  $\varepsilon$  < 1 for any cyclic heat engine.
- We shall encounter two other ways of stating the Second Law.

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### The Carnot Engine and its Efficiency: I

In 1824, Sadi Carnot considered a very particular engine cycle involving an ideal gas as the "working fluid." This <u>Carnot engine</u> has two great virtues:

- 1. It is relatively easy to calculate its efficiency.
- 2. More importantly, it turns out that the Carnot efficiency is the greatest possible efficiency for any engine cycle utilizing given temperatures ( $T_H$  and  $T_C$ ) for the "heat source" and the "heat sink."

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### The Carnot Engine and its Efficiency: II

In the Carnot engine, a fixed quantity of ideal gas follows the following four-stage cycle:

- Isothermal expansion at temperature T<sub>H</sub>
- Adiabatic expansion until T=T<sub>C</sub>
- Isothermal compression at temperature T<sub>C</sub>
- Adiabatic compression until T=T<sub>H</sub> & V = V<sub>init</sub>
   NOTE: To get a true <u>cycle</u> requires careful choice of the endpoints of the isothermal stages.

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### The Carnot Engine and its Efficiency: III

 Using the definition of efficiency, the first law of thermodynamics, and the ideal gas law, it is not difficult to show that the efficiency of the Carnot engine is

 $\varepsilon_{Carnot} = 1 - \frac{T_C}{T_H}$ 

• NOTE: Although the value of  $\epsilon$  is most easily calculated for a Carnot cycle that uses an ideal-gas working fluid, the same efficiency applies to ANY working fluid that cycles using these four stages.

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Absolute Zero

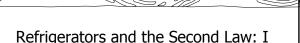
 From the expression for the Carnot efficiency, we can see that if we could use a heat sink at 0 K, we would have a perfect heat engine. Since the Second Law rules out perfect engines, we conclude that <u>it is impossible to achieve a temperature of 0 K</u>. This is often referred to as the <u>Third Law of</u>

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Thermodynamics.

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- Energy spontaneously moves from hot material to
- The purpose of a <u>refrigerator</u> is to accomplish the reverse: the transfer of energy from a cold reservoir to a bot one.
- A <u>cyclic refrigerator</u> accomplishes this with a "working fluid" that completes a closed cycle.
- The coefficient of performance of a refrigerator is

$$K \equiv \frac{|Q_C|}{|W_{by}|} = \frac{|Q_C|}{|W_{on}|}$$

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cold material.

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### Refrigerators and the Second Law: II

- A perfect refrigerator would transfer energy from cold matter to hot matter without the input of work.
- "Perfect refrigerators do not exist." (This is an alternative version of the Second Law.)
- A Carnot engine can be reversed and used as a Carnot refrigerator. Its coefficient of performance is

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

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# Reese Ch. 15, Part A2 (pp. 677-689)

- Carnot Efficiency as the Upper Limit for the Efficiency of a Real Heat Engine
- Coefficient of Performance of a Carnot Refrigerator as the Upper Limit for the Coefficient of Performance of a Real Refrigerator
- The Concept of Entropy
- Entropy and the Second Law
- Application: The Direction of Heat Flow

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Carnot Efficiency as the Upper Limit for the Efficiency of Real Heat Engines

- A Carnot engine is reversible.
- Suppose that a "super engine" exists, with ε>ε<sub>C</sub>.
  Then use it to run a Carnot refrigerator of just the correct size.
- Bundle the two inside a box and bingo, you have a perfect refrigerator, in contradiction to the 2<sup>nd</sup> Law.
- Therefore there can be no engine with  $\varepsilon > \varepsilon_C$

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# the Upper Limit for COP's of Real Refrigerators

- Suppose that a "super refrigerator" exists, with K>K<sub>C</sub>.
- Run this "super refrigerator" with a Carnot engine of just the correct size.
- Bundle the two inside a box and bingo, you again have a perfect refrigerator, in contradiction to the 2<sup>nd</sup> Law.
- Therefore there can be no refrigerator with K>K<sub>C</sub>.

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- CARNOT ENGINE: When the working fluid proceeds clockwise around a Carnot cycle, it receives |Q<sub>H</sub>| via heat transfer during the hot isothermal expansion and expels |Q<sub>C</sub>| during the cold isothermal compression.
- CARNOT REFRIGERATOR: When the working fluid proceeds counterclockwise around a Carnot cycle, it receives |Q<sub>c</sub>| via heat transfer during the cold isothermal expansion and expels |Q<sub>H</sub>| during the hot isothermal compression.
- In each case, the quantity  $\oint \frac{\delta Q}{T}$  equals zero!

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### Entropy: II

- By judicious combination of enough Carnot cycles (large and small), we can mimic essentially any closed path in the PV plane. Thus if we calculate  $\oint \frac{\delta \mathcal{Q}}{T}$  around ANY closed path in the PV plane, we get 0.
- In mechanics, when we encountered forces for which the work done around ANY closed path is 0, we were able to define a function of position called the "potential energy," such that

$$(PE_2) - (PE_1) = -\int_{anypath} \delta W$$

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Entropy: III

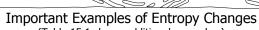
• Similarly, here we can define a quantity called the entropy (S) for which  $\delta O$ 

 $\Delta S \equiv S_2 - S_1 \equiv \int_{\substack{\text{anypath} \\ \text{from to 2}}} \frac{\delta Q}{T}$ 

### NOTES:

- S is a function of the thermodynamic equilibrium state. It appears that we could use any state as a reference state, for which S=0, but we'll see later that there is a natural choice.
- In analogy with  $\delta W_{by} = PdV$ , we have  $\delta Q = TdS$ .
- Inward heat transfer ("heat gain") increases a system's entropy; outward heat transfer ("heat loss") decreases it.

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## (Table 15.1 shows additional examples.)

• Ideal gas taken from state 1 to state 2:

$$\Delta S = nc_V \ln \left(\frac{T_2}{T_1}\right) + nR \ln \left(\frac{V_2}{V_1}\right)$$

• Melting or boiling:  $\Delta S = \frac{mL}{T}$ 

• Free expansion of an ideal gas: (This one deserves care!)

$$\Delta S = nR \ln \left( \frac{V_2}{V_1} \right)$$

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Entropy and the Second Law

 $\Delta S_{isolated} \ge 0$ 

• N.B.: A *nonisolated* system CAN show decreasing S.

• Although it's merely one application of the second law, notice that since (by definition?!) the universe is an isolated system:  $\Delta S_{universe} \geq 0$ 

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- If energy were to move from a cold reservoir to a hot one via heat transfer, that would cause the entropy of the universe to increase.
- Thus spontaneous heat transfer from hotter to colder regions can be thought of as a consequence of the Second Law.

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