Lecture 7, Sep 22, 2022

Converting Heat into Work

- Every gas has internal energy, so can we use the air to do work?
- Can we take Q from the air and convert this into W?
  - This does satisfy energy conservation
  - Of course, this is not possible, so why?
- A heat engine involves a heat source T_H, transferring heat Q_H to a gas to expand it, pushing a piston up
  - The engine stops when the temperature of the gas T reaches T_H
  - If we want the engine to do work again, we have to cool the gas, which requires a heat sink T_C
- As a consequence:
  1. To increase work, increase T_H
  2. In the limit $T_H \to T_C$, no work is done
  3. We always need 2 temperatures
- This implies that there is a "quality" of energy – just because something has internal energy, doesn't mean we can actually do useful work with it
  - The higher the temperature, the more work we can get out of it
- Can we define a property that measure this?
  - This would require some combination of the amount of energy and the temperature

Entropy and the Second Law

> **Definition**
>
> The fundamental property entropy S, where $\mathrm{d}S = \dfrac{\delta Q}{T}$, with units of J/K

- Entropy is an extensive property that changes when heat is added or remove from a system
- The entropy change is the ratio of the heat added and the temperature at which it was added
  - If δQ is added to a system, then T is the temperature of the boundary where the heat crossed
  - An increase in temperature decreases the entropy change
- Assume no work done so $\mathrm{d}U = \delta Q$, then the entropy change $\mathrm{d}S = \dfrac{\delta Q}{T}$
- $\Delta S = \displaystyle\int_1^2 \mathrm{d}S = \int_1^2 \frac{\delta Q}{T}$

> **Definition**
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> A thermal reservoir is a system whose temperature remains constant, even when heat is added or taken from it (think of a very large thermal mass, e.g. the air, a lake, etc)

- For a thermal reservoir, $\Delta S = \displaystyle\int_1^2 \frac{\delta Q}{T} = \frac{1}{T}\int_1^2 \delta Q = \frac{Q_{12}}{T}$
- Consider two thermal reservoirs A with $T + \Delta T$ and B with T (assume $\Delta T > 0$); bring them together and let them exchange heat
  - $\Delta S_A = \dfrac{Q}{T + \Delta T}$
  - $\Delta S_B = \dfrac{Q}{T}$
  - ΔS_B is greater in magnitude, so the total entropy increases (entropy generated is $S_{gen} = |\Delta S_B| - |\Delta S_A|$)
  - Note $\Delta T \to 0, \implies S_{gen} \to 0$
- Energy is conserved, but entropy can be generated

  - Entropy is generated when heat transfer occurs between two thermal reservoirs whose temperatures differ by a finite amount
  - All real heat transfer processes generate entropy
- Entropy cannot be destroyed, as that would involve a heat transfer from a lower temperature to a higher temperature
- Consider an isolated system not in equilibrium (system contains cold gas, and a little pocket of hot gas)
  - When the system goes to equilibrium, the heat from the hot pocket goes to the rest of the gas, so the entropy increases
- Doing work on a system does not change its entropy

Definition

The Second Law of Thermodynamics: The entropy an isolated system will increase until the system reaches equilibrium; the entropy of an isolated system remains constant

$\mathrm{d}S_{isolated} > 0$ when not in equilibrium; $\mathrm{d}S_{isolated} = 0$ when in equilibrium; $\mathrm{d}S_{isolated} < 0$ is impossible

- The second law defines what things happen spontaneously
- Example: a ball can be dropped and have its PE be lost to heat, but a ball on the ground can never spontaneously gain PE from the environment and lift up
  - If the ball spontaneously jumps into the air, heat has to be taken from the air, which decreases the entropy, violating the second law

Real Processes

- Real processes always produce entropy
- Consider a force pulling up a mass $F = mg$ at equilibrium
  - If we increase the force to $F + \Delta F$ in the limit as $\Delta F \to 0$, this would be a quasi equilibrium process and the mass is lifted up
  - If we reverse this process and make ΔF negative, then we can recover all the energy
  - For this reason the process is called *reversible*

Definition

Reversible process: Both the system and its surroundings can be put back into the initial state

- In a real system, heat is generated by friction in the pulley
  - Q is transferred to the surroundings, so the entropy of the surroundings increases
  - Even if the mass is lowered back, the entropy of the surroundings cannot be lowered again

Definition

Isentropic process: Quasi-equilibrium processes (reversible) without heat transfer or generation of entropy