Energy Devices – Thermodynamics (Lecture 5)

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Lecture outline:

- Kinetic theory of pressure.
- Operation of cyclic machines – the second law.
- Energy conservation – the first law.
- The zero'th law and driving a system to equilibrium.
- A physical picture of entropy.

"Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics. Perhaps it will be wise to approach the subject cautiously." – David Goodstein, *States of Matter*

"My greatest concern was what to call it. I thought of calling it 'information', but the word was overly used, so I decided to call it uncertainty. When I discussed it with John von Neumann, he had a better idea. Von Neumann told me, 'You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, *nobody knows what entropy really is, so in a debate you will always have the advantage.*" – between Claude Shannon and von Neumann[1]

[1] http://en.wikipedia.org/wiki/Entropy

Image sources:

Fig. 3	http://en.wikipedia.org/wiki/File:Joule%27s_Apparatus_%28Harper%27s_Scan%29.png.

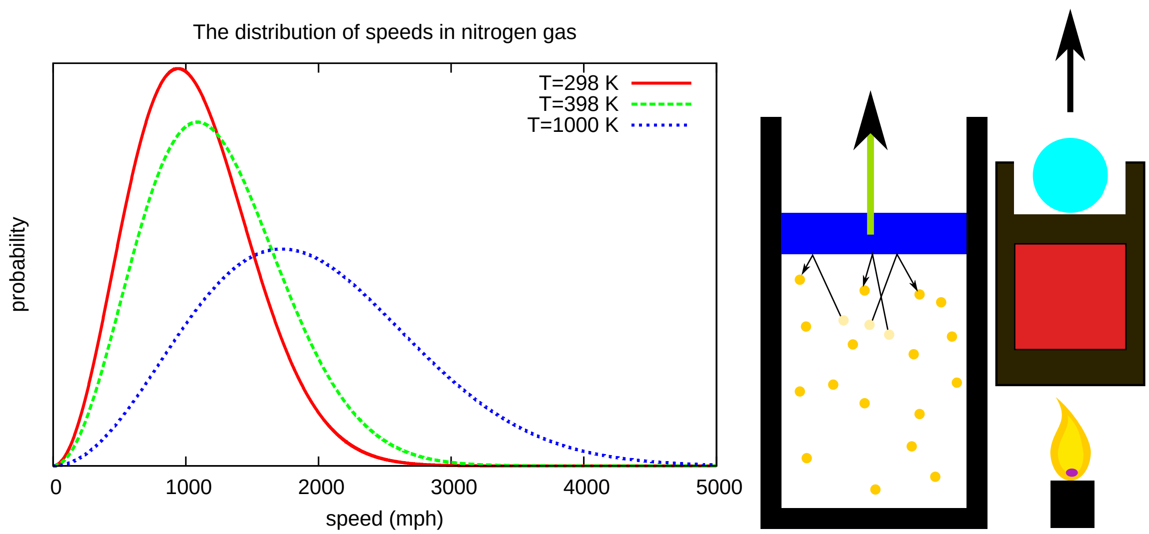

Figure 1: **Left:** the Maxwell-Boltzmann distribution of velocities as a function of temperature. As the temperature increases, the distribution moves out to higher velocity. This is because the mean kinetic energy ($E = (1/2)mv^2$) per particle has increased. The equipartition theorem states that the mean energy per particle is proportional to the energy scale of the temperature ($k_B T$, where $k_B = 1.3806504 \times 10^{-23}$ J/K) times the number of degrees of freedom in the gas divided by two. A monoatomic gas has three degrees of freedom (moving in three dimensions) so that $E = (3/2)k_B T$. **Middle:** the kinetic origin of pressure – air molecules bouncing off of a movable piston. Each bounce passes some momentum to the piston, and the net rate of momentum exchange with the piston becomes a force per unit area. This has units of pressure, like psi (pounds per square inch). **Right:** a thermodynamic lifter that uses heat from a candle to do mechanical work.

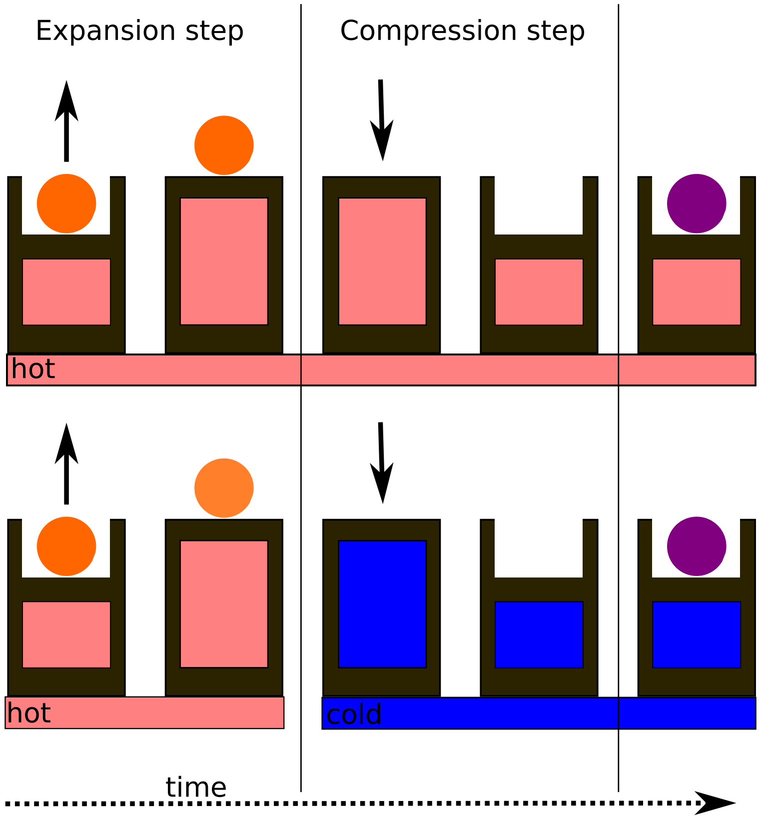

Figure 2: A rough schematic to motivate the second law of thermodynamics. To first lift the mass, the cylinder undergoes expansion at constant temperature driven by the heat flow from e.g. a candle. We would now like to reset the device so that we can use it again to lift another mass, and so must compress the piston. If we compress the piston at the same temperature, it will take all the work that the lifter just did in lifting the mass. Thus, the top sequence does no net work using the input thermal energy. To achieve some net work from a cycle, we need to cool the gas before compressing it again. After the gas is cool, it can be compressed at constant temperature using less work than was achieved in the expansion. Compressing the gas at constant temperature rejects heat to the cold plate. This device therefore converts heat from the hot side into *both* net mechanical work *and* some waste heat on the cold side, so not all of the heat can go into useful work. The Kelvin form of the second law: *A cyclic engine can not convert thermal energy into mechanical energy unless the devices uses two temperatures and discards heat to the cold side.* (More realistic engines will be described in the next lecture – this figure is only meant to show that one needs two temperatures and has a limited efficiency.)

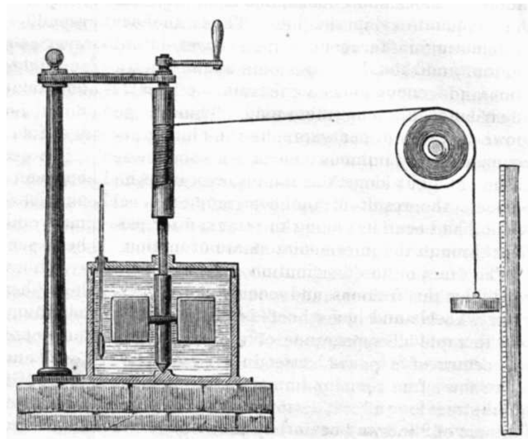

Figure 3: Joule's device showing the equivalence of mechanical and heat energy. A falling mass rotates a paddle. The drag on the paddle is dissipated as heat in the water, producing an increase in temperature. The BTU is the amount of energy required to raise one pound of water one degree Fahrenheit (analogous to the calorie) and the Joule describes the amount of mechanical potential energy embodied in the falling mass. This experiment demonstrates that both are valid, interconvertible units of energy (though BTU has imperial units and Joule is metric). The first law of thermodynamics is simply a statement of the conservation of energy: the change of the internal energy of a system is the amount of heat that is added to the system minus the work that it does. Note that while we expect the mass to fall and heat the water, *we do not expect hot water to cause the paddle to turn and lift the mass*. While heat and work have the same units, there is something fundamentally different between them.

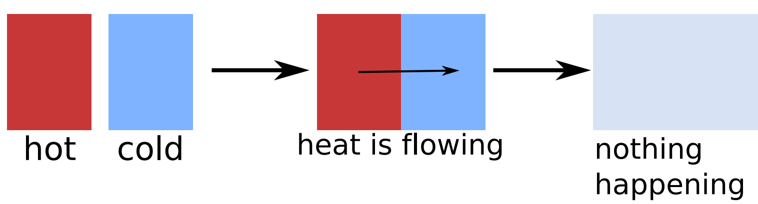

Figure 4: Heat flow driving equilibrium. When the hot and cold blocks make contact, the temperature gradient drives a heat flow until the two blocks equilibrate to the same temperature. The zero'th law of thermodynamics states that if system A is in equilibrium with system B and B is in equilibrium with C, then A is in equilibrium with C.

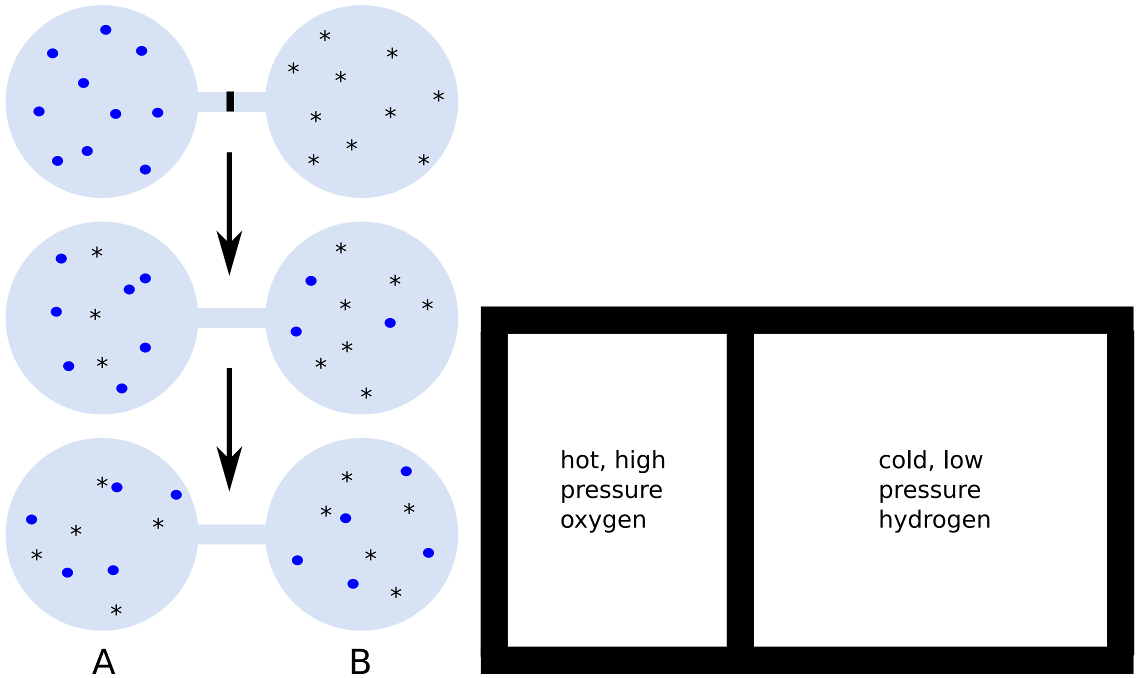

Figure 5: Fig. 4 shows equilibrium with respect to temperature gradients and heat flows, but there are several other types of equilibrium to consider. **Left:** two species mixing spontaneously. Here, once the stopcock is opened, the gradient in concentration drives a particle flow until the two species are equally mixed across the two bulbs. **Right:** a system with several equilibria. Consider several steps: 1) let the partition conduct heat, driving a heat flow until the temperatures on the two sides of the partition match, 2) allow the partition to move, so that the two compartments will reach mechanical equilibrium where the pressures on each side match, 3) make the partition porous so that the gases mix between the cylinders, 4) ignite the gases, so that a chain reaction drives the chemical equilibrium. In general, *gradients drive currents until equilibrium is reached*. A gradient in temperature reaches equilibrium through heat flow. A gradient in electrical potential moves charge through a current. A gradient in density or pressure moves particles in a flow. Equilibrium is reached when there are no gradients in the intensive variables (temperature, pressure, potential). These gradients are essential to energy technology! (See “Physics of Solar Cells” by P. Würfel for discussion of several equilibria.) Note that gradients may exist arbitrarily long: we may choose to never open the stopcock between the bottles (left figure). Also note that it is thermodynamically improbable that once the gases are mixed that they will ever unmix.

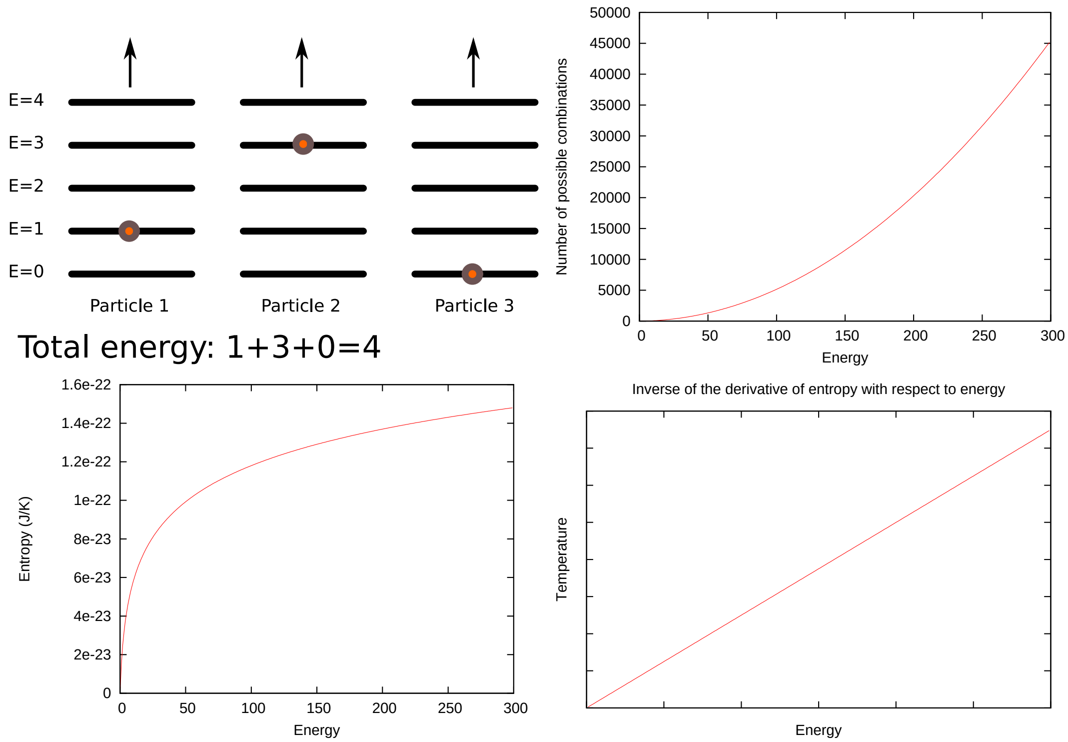

Figure 6: **Top left:** three particles which can have energy in integer units, $E = 1$ unit, $E = 2$, and so on, forming a ladder. At zero total energy, each particle must have zero energy, so there is only one way to distribute zero units of energy. For one unit of energy, there are three possible ways to distribute the energy: either particle 1, 2, or 3 may have that unit of energy. For two units of energy, there are six ways to distribute the energy. We will refer to the number of various allowable distributions of some total energy as the number of "accessible" states. As we add more energy to the system (heating it), the number of accessible states increases. **Top right:** The number of accessible states as a function of energy. **Bottom left:** The entropy has units of energy per temperature and is defined as k_B ($1.3806504 \times 10^{-23}$ J/K) times the natural log of the number of accessible states ("microstates"); written as $S = k_B \ln W$. **Bottom right:** The temperature is defined through $1/T = \partial S/\partial U$, ($\partial S/\partial U$ is the slope of the entropy as a function of energy) and can be interpreted as the inverse of the fractional change in the number of accessible states for some heat input. Turning this around, we reach the standard expression that $\Delta Q = T \Delta S$, the heat added is the temperature times the change in entropy. Summarizing: *entropy quantifies the dispersal of heat at temperature T.* Real systems will be more complicated, having for example 10^{23} particles instead of three, and the specification of possible energies will depend on the degrees of freedom of the particles. The above ladders are cooked up to show that the number of accessible states increases with heating, and that the temperature is related to the number of new states that become available for a given amount of heat.