Quick Review of Work, Heat, and the Second Law

The goal of this writeup is to briefly review in an intuitive, non-quantitative way some important principles governing transformations of energy. Our class focuses on the conversion of raw energy resources (thermal energy and chemical potential energy) into useful mechanical work. We are very interested in the efficiencies with which such transformations take place. Our work will be much easier if we have a few of these ideas present in the back of our heads as we go.

We define energy as being the sum of kinetic energy ($\frac{1}{2}mv^2$) and potential energy.

(Potential energy is generally considered as a force through a distance. Examples include a compressed spring or the energy contained in a chemical bond.) The total energy is a conserved property, meaning it cannot be created or destroyed, but only changed in form and moved in and out of systems. This leads to the idea behind the First Law. For a control volume:

Energy crossing boundary into CV – Energy leaving CV = Change in energy within CV

In thermodynamic systems we generally divide energy into (1) a component consisting of the energy associated with random molecular motions, and (2) the energy associated with organized motion of the mass. More specifically these are:

1. *Internal Energy.* This is the energy associated with the random molecular motion of the individual gas molecular. To the outside observer, the gas appears to be macroscopically at rest (*i.e.*, no observable kinetic energy). This is termed the *internal energy* of the gas, and is given the symbol "u". For molecular gases such as O_2, the internal energy also includes contributions from the rotation and vibration of the molecules. The internal energy is closely related to the observed temperature of the gas, and thus is often termed the *thermal energy* of the gas. In a system where chemistry can occur, the internal energy can contain the potential energy associated with the chemical bonds.

    Note that the internal energy of a simple monatomic gas is easy to calculate. You just sum the kinetic energy of all the atoms in the system:

    $$u = \sum_i m_i \frac{u_i^2}{2}$$

    This has limited practical utility as one cannot measure all the atomic velocities, but it does demystify the idea of internal energy somewhat.

2. *Organized Energy.* This is the energy associated with the bulk velocity of the gas. For example, if the *CV* is moving at 10 m/s, the overall *CV* will have this kinetic energy in addition to the internal energy. Another example would be a stationary *CV*

within which the gas is swirling. This "macroscopic" kinetic energy could be recovered as work (*e.g.*, by reversibly slowing the gas to zero velocity and storing the energy in a spring). Another term for this is the *organized energy*, since it involves that part of the molecular motion in which all the molecules are moving in the same direction at the same speed.

One simple statement of the Second Law is that spontaneous processes always tend to convert organized energy into disorganized energy. Imagine a frictionless pool table in which all the balls are initially going in the same direction at the same speed. One can easily expect that collisions between the balls will lead to a random distribution of speeds and directions. Alternately, one would expect that a random situation is very unlikely to spontaneously order itself such that all balls are moving at the same direction at the same speed. Thus we see that a work flow can be converted completely into disorganized energy (*e.g.*, rotating shaft work converted into heat during frictional drilling), but that disorganized internal energy cannot be completely recovered as organized work.

So far so good, but the next part gets a little tricky. It turns out that a flow of heat does contain a certain amount of "organization." Specifically, 1 kJ of heat extracted from a 1000 K body has more organization than 1 kJ of heat from a 500 K body. (The proof is in your thermo book. We are just after results here.) This allows us to make two important conclusions.

First, this says that heat will always flow from hot to cold. Specifically, 1 kJ of heat moving from 1000 K to 500 K will become more disorganized, which is an allowed process under the Second Law. The reverse process would spontaneously create "organization", which is not allowed.

The more important consequence is the heat engine. Consider a heat engine operating between two reservoirs:
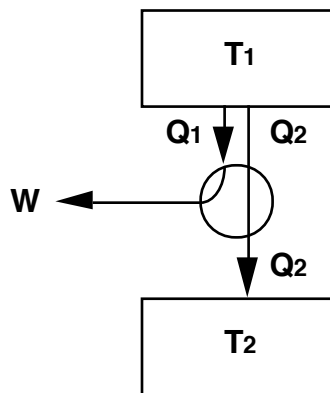
Here, Q_1 starts as disorganized energy at T_1, and is promoted to 100% organized energy as W. Q_2 starts as disorganized energy at T_1, and is demoted to a greater level of disorganization at T_2. In a reversible cycle, the promotion effect experienced by the W is exactly balanced by the demotion effect experienced by Q_2, and the net disorganization of the system remains the same after the cycle (*e.g.*, a Carnot cycle). In a real system, W is

less, and Q_2 is more, so the net disorganization increases. For a heat engine to work, both the promotion and demotion have to occur together. This is the only mechanism possible for extracting organized energy from disorganized energy.

The "disorganization" that is associated with energy is of course termed entropy, and this must always increase for isolated processes. A less familiar term is "availability", which refers to the potential of a thermodynamic resource to be converted to organized work. For example, a 10 kJ heat flow from a 1000 K reservoir could be put through a Carnot cycle. If the environment is at 300 K, the 10 kJ is converted into 7 kJ of work and 3 kJ of heat rejected to the environment. This means that the "availability" of the 10 kJ of heat is 7 kJ of work. We will deal extensively with this idea in the next handout.