The basic concepts of Thermodynamics

The basic abstraction of thermodynamics is the division of the world into *systems* delimited by real or ideal *boundaries*. The systems not directly under consideration are lumped into the *environment*. It is possible to subdivide a system into subsystems, or to group several systems together into a larger system. Usually systems can be assigned a well-defined *state* which can be summarized by a small number of parameters.

Thermodynamic Systems

A thermodynamic system is that part of the universe that is under consideration. A real or imaginary boundary separates the system from the rest of the universe, which is referred to as the *environment*. A useful classification of thermodynamic systems is based on the nature of the boundary and the flows of matter, energy and entropy through it.

There are three kinds of systems depending on the kinds of *exchanges* taking place between a system and its environment:

- *isolated* systems: not exchanging heat, matter or work with their environment. An example of an isolated system would be an insulated container, such as an insulated gas cylinder.
- *closed* systems: exchanging energy (heat and work) but not matter with their environment. A greenhouse is an example of a closed system exchanging heat but not work with its environment. Whether a system exchanges heat, work or both is usually thought of as a property of its boundary, which can be
    - *adiabatic* boundary: not allowing heat exchange;
    - *rigid* boundary: not allowing exchange of work.
- *open* systems: exchanging energy (heat and work) and matter with their environment. A boundary allowing matter exchange is called *permeable*. The ocean would be an example of an open system.

In reality, a system can never be absolutely isolated from its environment, because there is always at least some slight coupling, even if only via minimal gravitational attraction.

In analyzing an open system, the energy into the system is equal to the energy leaving the system. [1] (*http://www.tpub.com/content/doe/h1012v1/css/h1012v1_94.htm*)

Thermodynamic state

A key concept in thermodynamics is the *state of a system*. When a system is at equilibrium under a given set of conditions, it is said to be in a definite *state*. For a given thermodynamic state, many of the system's properties have a specific value corresponding to that state. The values of these properties are a function of the state of the system and are independent of the path by which the system arrived at that state. The number of properties that must be specified to describe the state of a given system is given by Gibbs phase rule. Since the state can be described by specifying a small number of properties, while the values of many properties are determined by the state of the system, it is possible to develop relationships between the various state properties. One of the main goals of Thermodynamics is to understand these relationships between the various state properties of a system. Equations of state are examples of some of these relationships.

The Laws of Thermodynamics

Alternative statements that are mathematically equivalent can be given for each law.

- **Zeroth law**: *Thermodynamic equilibrium*. When two systems are put in contact with each other, energy and/or matter will be exchanged between them unless they are in thermodynamic equilibrium. Two systems are in thermodynamic equilibrium with each other if they stay the same after being put in contact. The zeroth law is stated as

  If A and B are in thermodynamic equilibrium, and B and C are in thermodynamic equilibrium, then A and C are also in thermodynamic equilibrium.
  While this is a fundamental concept of thermodynamics, the need to state it explicitly as a law was not perceived until the first third of the 20th century, long after the first three laws were already widely in use, hence the zero numbering. There is still some discussion about its status.
  Thermodynamic equilibrium includes *thermal equilibrium* (associated to heat exchange and parameterized by temperature), *mechanical equilibrium* (associated to work exchange and parameterized generalized forces such as pressure), and *chemical equilibrium* (associated to matter exchange and parameterized by chemical potential).

- **1st Law**: *Conservation of energy*. This is a fundamental principle of mechanics, and more generally of physics. In thermodynamics, it is used to give a precise definition of heat. It is stated as follows:

  The work exchanged in an adiabatic process depends only on the initial and the final state and not on the details of the process.
  or
  The heat flowing into a system equals the increase in internal energy of the system minus the work done by the system.
  or
  Energy cannot be created, or destroyed, only modified in form.

- **2nd Law**: A far reaching and powerful law, it can be stated many ways, the most popular of which is:

  It is impossible to obtain a process such that the unique effect is the subtraction of a positive heat from a reservoir and the production of a positive work.
  Specifically,

A system operating in contact with a thermal reservoir cannot produce positive work in its surroundings (Lord Kelvin)
or
A system operating in a cycle cannot produce a positive heat flow from a colder body to a hotter body (Clausius)
The entropy of a thermally isolated macroscopic system never decreases (see Maxwell's demon), however a microscopic system may exhibit fluctuations of entropy opposite to that dictated by the second law (see Fluctuation Theorem).

- **3rd Law**: This law explains why it is so hard to cool something to absolute zero:

  All processes cease as temperature approaches zero.
  As temperature goes to 0, the entropy of a system approaches a constant

These laws have been humorously summarised as Ginsberg's theorem: (1) you can't win, (2) you can't break even, and (3) you can't get out of the game.

Or, alternatively: (1) you can't get anything without working for it, (2) the most you can accomplish by working is to break even, and (3) you can only break even at absolute zero.

Or, (1) you can't get out more than you put in (2) even the best-designed machine eventually loses energy and stops (3) you can't get to absolute zero.

Or, (1) you cannot win or quit the game, (2)you cannot have a tie in the game unless it is very cold, (3) the weather doesn't get that cold.

More about the 2nd Law

The Second Law is exhibited (coarsely) by a box of electrical cables. Cables added from time to time tangle, inside the 'closed system' (cables in a box) by adding and then removing cables. The best way untangle is to start by taking the cables out of the box and placing them stretched out. The cables in a closed system (the box) will never untangle, but giving them some extra space starts the process of untangling (by going outside the closed system).

C.P._Snow said the following in a Rede Lecture in 1959 entitled "The Two Cultures and the Scientific Revolution."

"A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold: it was also negative."