Thermodynamics – The Three Laws and Entropy

Thermal equilibrium – two bodies are said to be in thermal equilibrium if, when connected to each other, their combined thermal state (temperature) is the same as their individual thermal states (temperatures).

The Zeroth Law of Thermodynamics gives the important property of *temperature*.

If bodies A and B are in thermal equilibrium with a third body C, then A and B are in thermal equilibrium with each other.

Think of the "third body C" as the thermometer, the instrument for measuring temperature.

Heat is defined as a quantity of energy. It is most commonly measured in calories, but can be expressed as joules (mks), ergs (cgs) or btus (english).

1 calorie = energy required to raise the temp of 1 gram of water from 14.5°C to 15.5°C

The First Law of Thermodynamics expresses the conservation of energy with respect to a thermal system and the heat it absorbs and the work it does. Remember that work is force times distance and has the same units as energy.

$$\Delta U = Q - W$$

ΔU = change in internal energy (kinetic, potential and heat) of the system
Q = heat energy input to the system (can be + or -)
W = work done by the system (can be + or -)

The First Law says nothing about temperature. What we really need is a law that relates heat energy (Q) input to the system, work (W) done by the system and the temperature (T) of the system. The Second Law of Thermodynamics brings temperature into the picture and, in doing so, informs us of universal limitations of physical systems. It also gives us an indication of which direction a natural process will take. For example, the Second Law tells us that heat energy will always flow from a warmer body to a colder body, never the other way.

The physical quantity employed in the Second Law is entropy. Entropy may be thought of as a measure of the ability of a system to do work. However, this is somewhat confusing because the system's ability to do work <u>decreases</u> as the entropy of the system <u>increases</u>. More confusing is the fact that entropy (S) is defined as a differential rather than as an integral. Here's the definition.

$$dS = dQ/T$$

dS = a small change to the entropy of a system

dQ = a small change to the heat input to the system
T = the absolute temperature of the system

What is of interest is the change in the value of S (the entropy) for a system and for the universe when a system goes from one state of thermal equilibrium to another. The Second Law of Thermodynamics states that

A natural process always takes place in such a direction as to cause an increase in the entropy of the system plus environment. In the case of an isolated system, it is the entropy of the system that tends to increase.

In what is called a "reversible" process, where the state transition takes place as an infinite number of infinitesimal intermediate states of thermal equilibrium, the change in entropy can be expressed as an integral equality.

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T}$$

For an "irreversible" process, where the state transition involves states of thermal non-equilibrium

$$\Delta S = S_2 - S_1 > \int_1^2 \frac{dQ}{T}$$

For an isolated system, where $dQ = 0$,

$S_2 = S_1$ for a reversible system, and

$S_2 > S_1$ for an irreversible system.

An implication of the Second Law is that in every thermal state transition for a physical system, the entropy of the universe either remains the same or increases. It never decreases.

Some comments on entropy and the Second Law.

1.The entropy of a system is defined for equilibrium states only.

2. The entropy of a system in equilibrium is independent of its past history.

3. For practical problems, we are generally only interested in changes in entropy. For convenience, the entropy of a substance may be assumed zero in some convenient reference state and a numerical value can then be assigned to the entropy in any other state. Tables of such values have been prepared. For example, the entropy of water is assumed zero when it is in the liquid phase at 0°C and 1 atm pressure and values are

tabulated for the entropy over a wide range of temperatures and pressures, in the vapor as well as in the liquid phase. Such tables can be used in determining changes in entropy for reversible or irreversible processes.

4. Entropy is an extensive property of the system, proportional to its mass or number of moles.

5. The Second Law of Thermodynamics is not an absolute law, like the First Law, which is true under all circumstances. At the microscopic level, where small numbers of molecules are involved, the Second Law must be expressed using probability, where there is a small, although nonzero, probability of a violation of the law.

Two illustrative problems from the Halliday and Resnick textbook.

1. Compute the entropy change when 1 kg of ice at 0°C (=273°K) melts to water at 0°C, taking the latent heat of melting of ice to be 79.6 cal/gm.

$$S_{water} - S_{ice} = \int_0^Q \frac{dQ}{T} = \frac{1}{T} \int_0^Q dQ = \frac{Q}{T}$$

$$Q = 10^3 \text{gm} * 79.6 \text{ cal/gm} = 7.96 * 10^4 \text{ cal}$$

$$S_{water} - S_{ice} = \frac{7.96 \times 10^4}{273} \text{ cal/}°K = 292 \text{ cal/}°K$$

In the process of melting, the ice takes heat from the surroundings which must be at a temperature above 0°C. The gain in entropy of the ice exceeds the loss in entropy of the surroundings, so that the process as a whole involves an increase in the entropy. To reverse the process, that is, to freeze water, would require that heat be conducted from the water to a body at a temperature below 0°C. For such a system (water + cold body) the total entropy would again increase.

2. Calculate the entropy change that N moles of an ideal gas undergoes in a reversible isothermal [i.e. heat is added to keep constant temperature] expansion from a volume V_i to a volume V_f.

Recall that for an ideal gas $pV=NRT$, where

p = pressure (atm)
V = volume (l)
N = number of moles
R = 1.986 cal/mole-°K
T = temperature (°K)

Pressure times change in volume (p times ΔV) is the work done by the gas. The First Law, expressed as differentials, becomes

3

$$dU = dQ - pdV = 0$$

dU = 0 because U depends only on temperature for an ideal gas, and T is constant.

$$dQ = pdV$$

$$dS = \frac{dQ}{T} = \frac{pdV}{T} = \frac{NRTdV}{VT} = NR\frac{dV}{V}$$

$$S_f - S_i = \int_{V_i}^{V_f} NR\frac{dV}{V} = NR\ln\frac{V_f}{V_i} \quad \text{[ln means natural logarithm]}$$

Since $V_f > V_i$, $S_f > S_i$ and the entropy of the gas increases.

In order to carry out this process we must have a reservoir at temperature T which is in contact with the system and supplies the heat to the gas. Hence the entropy of the reservoir decreases by

$$\int_{V_i}^{V_f} \frac{dQ}{T} = NR\ln\frac{V_f}{V_i}$$

so that in this process the entropy of system + environment does not change. This is characteristic of a reversible process.

References:

Halliday, David and Robert Resnick, *Physics for Students of Science and Engineering*, Combined Edition, John Wiley & Sons, 1963.

Sears, Francis Weston, *An Introduction to Thermodynamics, the Kinetic Theory of Gases and Statistical Mechanics*, Second Edition, Addison-Wesley Publishing Company, Inc. 1964.