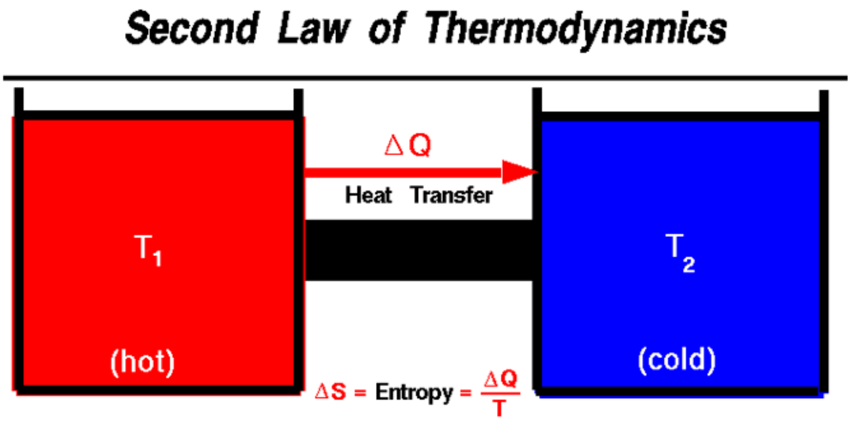
Lecture seven
The second law of thermodynamics

2nd Law of Thermodynamics

- 2nd Law introduces entropy, S

$dS = \frac{dq}{T}$ (Reversible) $\quad\quad dS > \frac{dq}{T}$ (Irreversible)

- Some of the enthalpy in a system is not convertible into work (PdV work for instance) because it is consumed by an increase in entropy
- Which could be restated that is requires some amount of work to increase entropy



NEED FOR THE SECOND LAW

- The First Law of Thermodynamics tells us that during any process, energy must be conserved.
- However, the First Law tells us nothing about in which direction a process will proceed spontaneously.
- It would not contradict the First Law if a book suddenly jumped off the table and maintained itself at some height above the table.
- It would not contradict the First Law if all the oxygen molecules in the air in this room suddenly entered a gas cylinder and stayed there while the valve was open.

MEANING OF ENTROPY AND THE SECOND LAW

- Entropy is a measure of the disorder (randomness) of a system. The higher the entropy of the system, the more disordered it is.
- The second law states that the universe always becomes more disordered in any real process.
- The entropy (order) of a system can decrease, but in order for this to happen, the entropy (disorder) of the surroundings must increase to a greater extent, so that the total entropy of the universe always increases.

Constant pressure	$w = -P_{ex}\,\Delta V$	$\Delta U = q + w$
Constant volume	$w = 0$	$\Delta U = q$
Isothermal (constant temperature)	$w = -q$	$\Delta U = 0$
Adiabatic (no heat flow)	$w = \Delta U$	$q = 0$

Entropy quotes

- "There is a great difference between energy and availability of energy. The availability of energy is always decreasing. This is called the entropy law, which says the entropy is always increasing." – Richard-Feynman
- "The thermodynamic sense of order decrease that is enshrined in the second law is at first sight in conflict with many of the complicated things that we see going on around us. We see complexity and order increasing with time in many situations: when we tidy up our office, the evolution of complex life-forms from the simpler ones.

In many of these cases, we must be careful to pay attention to all the order and disorder that is present in the problem. Thus the process of tidying the office requires physical effort on someone's part. This causes ordered biochemical energy stored in starches and sugars to be degraded into heat. If one counts this into the entropy budget, then the decrease in entropy or disorder associated with the tidied desk is more than compensated for by the other increases." Barrow (1990).

Combining the 1st and 2nd Laws of Thermodynamics:

$dU = dq_{rev} + dw = TdS – PdV$

If a process is at constant volume, V, and entropy, S → dU = 0 → nothing happens, energy does not change in the system

This is EQUILIBRIUM:

dU > 0 → spontaneous **rxn** products to reactants

dU < 0 → spontaneous **rxn** reactants to products

Third law of Thermodynamics:

- No system can reach absolute zero
- This is one reason we use the Kelvin temperature scale. Not only is the internal energy proportional to temperature, but you never had to worry about dividing by zero in an equation!
- All reactions in a liquid or solid in internal equilibrium take place with no change in entropy.
- There is no formula associated with the 3rd Law of Thermodynamics