Lecture 13

<u>The Second Law</u>

<u>Last Time</u>

Consequences of an Ideal Gas Internal Energy a Function of T Only

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A New State Function for Any System: Enthalpy $H = U + PV$

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A New State Function for an Ideal Gas System: Entropy

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Another State Function: Helmholtz Free Energy: $F = U - TS$

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Another and Friendly State Function: Gibbs Free Energy: $G = U - TS + PV$

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The Second Law of Thermodynamics

Finally, the second law (it is really an axiom—it has never been proved; only never disproved.)

There are quite a few equivalent ways to state the second law. If the statements are correct, they are all equivalent. Some are harder to understand than others; some are included only for historical purposes. I think the following way of stating the second law is useful.

A Every thermodynamic system possesses an extensive state function called "the entropy" which can be calculated by a reversible (that is, a quasi-static limit of a real process) path from an arbitrarily chosen "Reference State" by integrating the heat absorbed by the system divided by the absolute temperature of the system.

In other words, **"Entropy, the state function, exists for every system..."**

B During any observable process, the entropy of a system plus its surroundings (together defining an isolated system or universe) never decreases.

And, in other words, **"...and it always increases for the universe"**

─────────── **An Illustrative Example** ───────────────────────

Consider the passage of heat from a hot body to a cold one, with no other work being performed.

Consider two <u>very</u> large bodies, one at $T = 400$K and the other at $T = 300$K (The bodies are so BIG that there temperatures are roughly constant for the passage of a small amount of heat between them.)

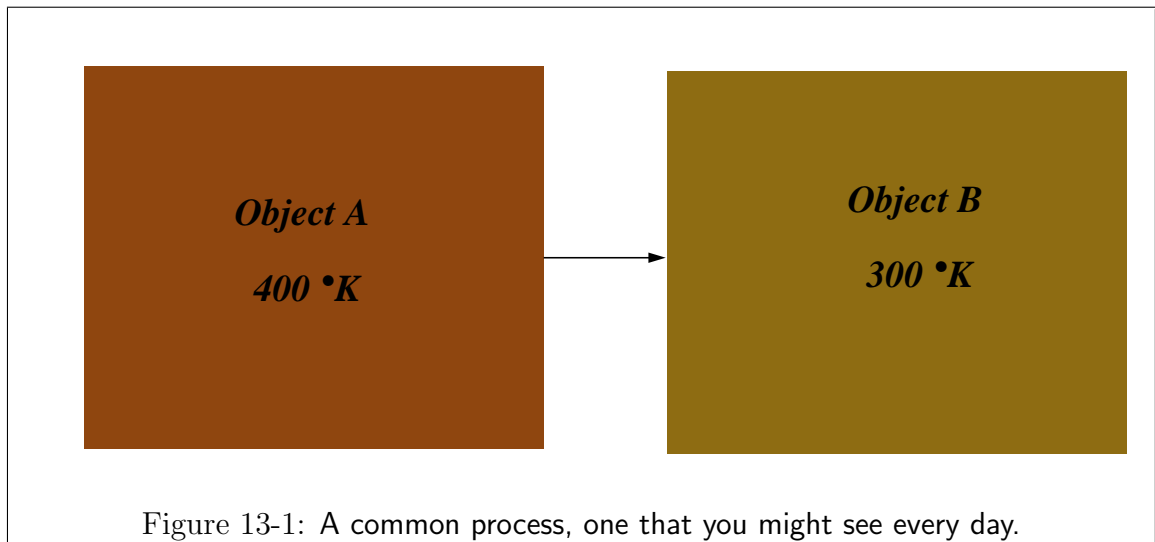Figure 13-1: A common process, one that you might see every day.

Case 1 Suppose 400 joules of heat are transferred from the hot object A to the cooler object B.

System A	System B
First Law $\Delta U_A = -400$J	$\Delta U_B = +400$J
Second Law $\Delta S_A = \frac{-400}{400}\frac{\text{J}}{\text{°K}}$	$\Delta S_B = \frac{+400}{300}\frac{\text{J}}{\text{°K}}$

$$\Delta S_{\text{universe}} = \Delta S_A + \Delta S_B = -1 + \frac{4}{3} = \frac{1}{3}\frac{\text{J}}{\text{°K}} \tag{13-1}$$

Case 2 Suppose that, somehow, the same amount of heat (400 J) is transferred from the cooler to the hotter body.

$$\Delta S_{\text{universe}} = -\frac{1}{3}\frac{\text{J}}{\text{°K}} \tag{13-2}$$

This is not observed.

Suppose that the bodies in Figure 13-1 are not so BIG this time and that they have a finite heat capacity, but suppose that the thermal conductivity of each body alone is very large compared to the thermal conductivity of the "stuff that allows heat to transfer between them." In other words, while heat flows between the bodies, we can consider the temperature of the bodies to be uniform at all times.

Using the definition of entropy and the heat capacities of each body, how should the entropy change of the universe be calculated?

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Alternative Statements of the Second Law (There are many)

Clausius Heat is not observed to pass spontaneously from a body at low temperature to a body at higher temperature.

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Kelvin It is impossible to continuously perform work by cooling a body to a temperature below that of the lowest temperature of its surroundings.

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Ostwald A perpetual motion machine "of the second kind" has never been observed. (A perpetual motion machine of the second kind "runs forever.")[15]

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Caretheodory This is the most elegant (and hardest to understand and apply, perhaps) as it requires the fewest underlying assumptions.

In the neighborhood of every thermodynamic state that can be reached by a reversible path, there exists states which cannot be reached along a reversible adiabatic (isentropic) path; or, in other words, which can be reached either irreversibly or not at all.

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[15]A perpetual motion machine "of the first kind" has never been observed (first law, a perpetual motion machine is one that creates energy continuously)

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MIT 3.00 Entropy is a state function that exists for every physical system and has the property that, when all associated systems are considered footnote The *universe* of a process. the sum of all the entropy changes is greater than or equal to zero.

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