Physics 161: Thermodynamics
Lecture #10

(Part of this lecture was delivered on Friday, 2/11/22, as in-class lecture 11.
The rest will be delivered as part of the lecture on Monday 2/14/22.)

The Free Energy, the Generalized Free Energy, and the Maximum Work

("die Entropie der Werlt streβt einem Maximum zu")

As proved in the Lecture 9 notes, systems evolve on their own (i.e. spontaneously) in such a manner as to increase $S_{\mathrm{univ.}}$. It is said that this implies that equilibrium is reached as $S_{\mathrm{univ.}}$ *tends to a maximum*. Here is the logic behind this statement. When $S_{\mathrm{univ.}}$ is at a maximum, there can be no further spontaneous evolution of the system to yet another state, because any further spontaneous evolution would imply yet another increase in $S_{\mathrm{univ.}}$. This would raise S_{univ} to a higher value, which could only happen if the initial value of $S_{\mathrm{univ.}}$ was not actually the maximum in the first place.

It sounds nonintuitive to say that equilibrium is determined by maximizing $S_{\mathrm{univ.}}$, or maximizing anything, for that matter. Part of the problem is that most of us have grown accustomed to making the casual statement that "mechanical systems evolve in order to minimize their energy". We say that bouncy balls stop bouncing when their energy goes to zero. We say that masses connected to springs stop oscillating and come to rest at the location $x = 0$ which forms the minimum of the potential energy $U(x) = \frac{1}{2}kx^2$. It is not that mechanical energy is "lost", however, but that it is transferred to the surroundings, as heat. By the first law, the total energy of the system and the surroundings together should be unchanged. Indeed, what we are seeing when we observe the evolution to equilibrium is not a loss of energy, but rather a *transfer* of energy. In the initial state all of the energy is in the oscillating mass. In the final state there will be an increase in the kinetic energy of the air molecules that surround the oscillating mass (or the internal motion of the atoms in the spring as it heats up while being stretched and compressed), while the mass itself comes to rest. What is it in nature that gives preference to energy leaving the oscillating mass and going into the environment, rather than energy leaving the environment and going into the oscillating mass? The entropy of the universe is the quantity that addresses the direction of the energy transfer. The entropy of the universe increases when the energy leaves the oscillator and goes into the surroundings. The entropy of the universe decreases when the energy leaves the surroundings and goes into the oscillator. In the last lecture we proved that only the former is possible.

We have calculated $\Delta S_{\mathrm{univ.}}$ for a number of different examples of spontaneous processes, and observed how it always increases. It turns out, however, that we can define another state function that is proportional to the negative of the entropy of the universe *under certain conditions*, and therefore goes to a

minimum when the entropy of the universe goes to a maximum. The usefulness of this new state function, called the *free energy*, is the subject of today's lecture.

1 Helmholtz's Free Energy A

Consider the state function A which is cobbled together from the state functions U, T, and S in the following manner,

$$A \equiv U - TS$$

This combination of state variables is called the "Helmholtz free energy", and it is a useful indicator of equilibrium when processes take place at constant T, and an situations where $W = 0$ (such as constant V for a fluid), for then it is directly proportional to $\Delta S_{\text{univ.}}$. On the other hand, it can also be used as a predictor of the maximum work that can be extracted from a process, assuming one is clever enough to devise a method to extract it.

Let's take a look at this. Consider the change in the Helmholtz free energy for some process,

$$\begin{aligned} \Delta A &= \Delta U - \Delta(TS) \\ &= (Q - W) - T\Delta S. \end{aligned}$$

In moving from the first line to the second line you can see that we have used the first law to substitute $Q - W$ for ΔU. We have also written $\Delta(TS) = T\Delta S$ since we are assuming an isothermal process. Let us now set $W = 0$ assuming that the process takes place while doing no work on the surroundings. Since $Q = -Q_{\text{surr}} = -T\Delta S_{\text{surr}}$, it follows that

$$\begin{aligned} \Delta A &= --T\Delta S_{\text{surr}} - T\Delta S \\ &= -T\Delta S_{\text{univ}}.(\text{constant } T, V) \end{aligned}$$

We see that when ΔS_{univ} is positive, ΔA will be negative. Thus we can restate the criteria for equilibrium as follows: When $W = 0$, *and* T is constant, *a system will evolve to minimize its Helmholtz free energy.* Let us look at two examples.

Example 1: A 2 liter vessel is divided in two halves by a rigid wall. On the left is 1 mole of ideal gas, in thermal contact with the surroundings at a temperature $T = 273$ K. The right has been evacuated. A small hole in the wall is sealed with a valve. When the valve is opened, x moles of gas move to the right half of the vessel, and $1 - x$ moles of gas remain on the left. (Although we know from experience that $x = 0.5$ when equilibrium is reached, with half the gas being on the left, and the other half of the gas being on the right, we will pretend that we don't know.) Calculate ΔA for the process, and make a graph of ΔA versus x. What is the value of x for which ΔA reaches a minimum?

Solution: If we consider the system to be the entire vessel, then this irreversible expansion is a process taking place at constant T and V, and as we
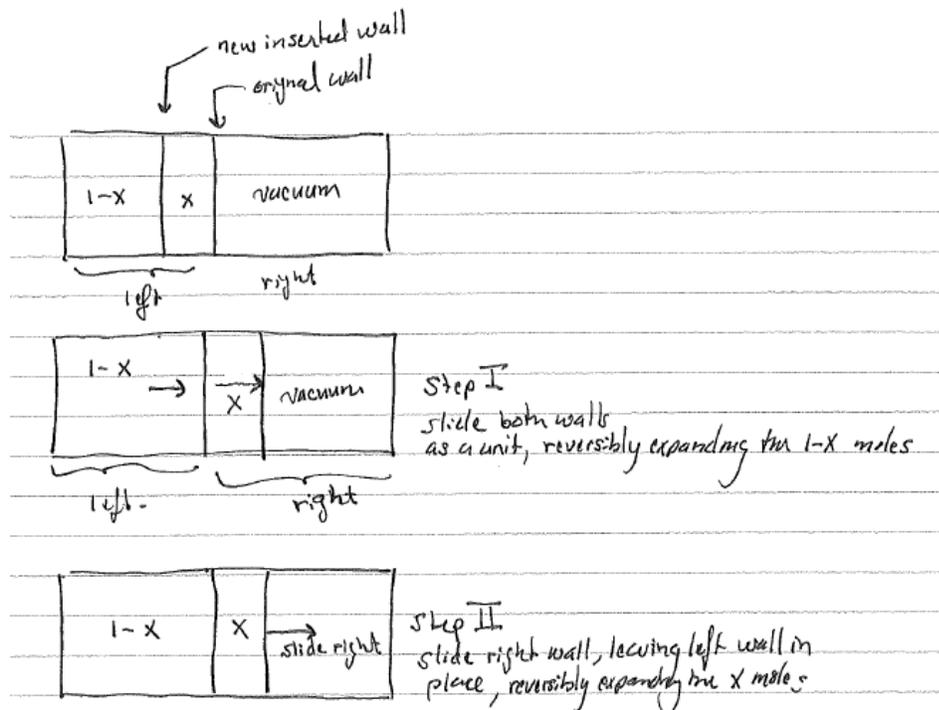
have proved above, under these conditions, A will proceed to a minimum as S_{univ} proceeds to a maximum. By definition, $A = U - TS$. At constant T, $\Delta A = \Delta U - T\Delta S$. To calculate ΔA, we must calculate ΔU and ΔS. In this case $\Delta U = 0$ because U only depends on T for an ideal gas, and T doesn't change. That leaves ΔS to be calculated. To calculate ΔS we can imagine a reversible process by which x moles of gas are moved from the left side to the right side. Here is one hypothetical reversible process that can bring the gas to its final state:

Imagine inserting a second wall on the left side of the container, partitioning the gas into two compartments, one with a volume of $1 - x$ liters, and the other with a volume of x liters. The $1 - x$ liter volume will contain $1 - x$ moles of gas. The x liter volume will contain x moles of gas. Next, slowly slide the second wall and the first wall together to the right, allowing the $1 - x$ moles to do reversible work in expanding to a volume of 1 liter. For this step, the work is given by

$$
\begin{aligned}
W_I &= \int PdV = nRT\ln\left(\frac{V_2}{V_1}\right) \\
&= (1 - x) \cdot R \cdot T \cdot \ln\left(\frac{1}{1 - x}\right) \\
&= -RT(1 - x)\ln(1 - x)
\end{aligned}
$$

Next, expand the compartment with a volume of x liters, holding x moles of gas, to a volume of 1 liter. For this step, the work is given by

$$
\begin{aligned}
W_{II} &= \int PdV = nRT\ln\left(\frac{V_2}{V_1}\right) \\
&= x \cdot R \cdot T \cdot \ln\left(\frac{1}{x}\right) \\
&= -RTx\ln(x)
\end{aligned}
$$

new inserted wall

orynal wall

1−x | x | vacuum

left | right

1−x → | x | vacuum

Step I
slide both walls
as a unit, reversibly expanding the 1−x moles

left | right

1−x | x | slide right

Step II
slide right wall, leaving left wall in
place, reversibly expanding the x moles

These two reversible isothermal expansions bring the system to the final state in which $1 - x$ moles of gas remain on the left, and x moles of gas are on the right. Since $\Delta U = 0$ for this hypothetical reversible path, then $Q = W_I + W_{II}$. Since this is reversible and isothermal, it follows that

$$\Delta S = \frac{Q_{\text{rev}}}{T} = -R\left[(1-x)\ln(1-x) + x\ln(x)\right]$$

Substituting ΔS into the expression for $\Delta A = \Delta U - T\Delta S$, we obtain the answer:

$$\begin{aligned}\Delta A &= RT\left[(1-x)\ln(1-x) + x\ln(x)\right] \\ &= 2.27\text{kJ}\left[(1-x)\ln(1-x) + x\ln(x)\right]\end{aligned}$$

At this point, we can ask, for what value of x will ΔA reach a minimum? To answer this, let us simply* make a graph of ΔA versus x.

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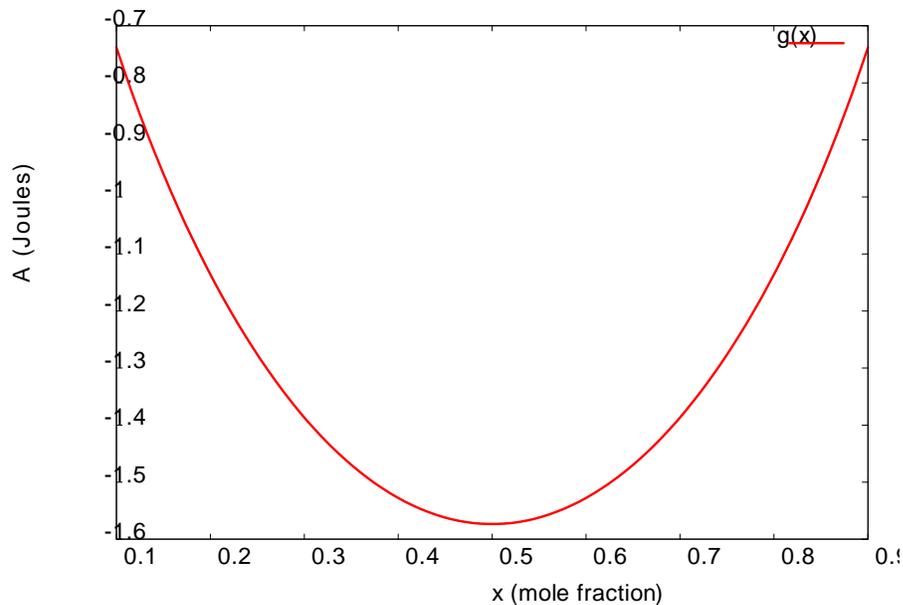
As you would expect, it is the value $x = 0.5$ that minimizes the Helmholtz free energy at constant T and V, telling us that, in equilibrium half of the gas is on the left side of the container, and the other half of the gas is on the right. The change in free energy for the process is therefore given by evaluating ΔA at $x = 0.5$. We have,

$$
\begin{aligned}
\Delta A &= 2.27\text{kJ} \cdot 2 \cdot (0.5)\ln(0.5) \\
&= -2.27 \text{ kJ} \cdot \ln(2) \\
&= -1.57 \text{ kJ}
\end{aligned}
$$

Example 2: Consider two one-liter glass bulbs connected by a narrow tube and closed with a stopcock, in thermal contact with the surroundings at 273 K. Initially, one mole of ideal gas is in the left bulb, and the right bulb is evacuated. When the stopcock is opened, the gas on the left rushes through the tube to fill the vacuum on the right. If a small propeller is inserted into the tube, so that the gas is forced to turn a propeller as it rushes by, what is the maximum amount of work that can be extracted from the system?
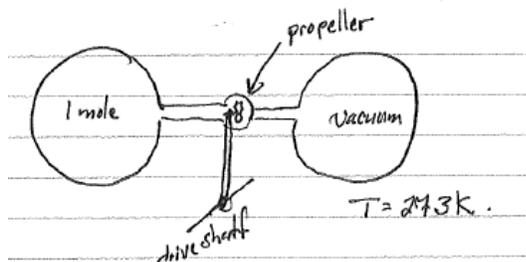
Solution: The system has been set up to be identical to the system in Example 1, except for the insertion of the propeller. It is a process that takes place at constant T and V, if we define our system to include both bulbs together. But $W \neq 0$ because of the insertion of the propeller, so it doesn't fit into the criterion for A that we described above, so it will be interesting to see where this takes us. Start with the definition $A = U - TS$. At constant T,

$$\Delta A = \Delta U - T\Delta S$$

Now, using the first law, we write

$$\begin{aligned} \Delta U &= Q - W_{\text{propeller}} \\ &= -T\Delta S_{\text{surr}} - W_{\text{propeller}} \end{aligned}$$

Inserting the expression for ΔU into the expression for ΔA, we have

$$\begin{aligned} \Delta A &= -T\Delta S_{\text{surr}} - W_{\text{propeller}} - T\Delta S \\ &= -T\left(\Delta S_{\text{surr}} + \Delta S\right) - W_{\text{propeller}} \\ &= -T\Delta S_{\text{univ}} - W_{\text{propeller}} \end{aligned}$$

Solving for $W_{\text{propeller}}$, we have

$$\begin{aligned} W_{\text{propeller}} &= -\Delta A - T\Delta S_{\text{univ}} \\ &= 1.57\text{kJ} - T\Delta S_{\text{univ}} \end{aligned}$$

What is $T\Delta S_{\text{univ}}$? We can see from the expression above that when there is no propeller, $W_{\text{propeller}} = 0$, and $T\Delta S_{\text{univ}} = -\Delta A = 1.57\text{kJ}$ is given by the negative of the change in the state function ΔA. Insertion of the propeller will not change the value of ΔA since the initial and final states of the gas will be the same with or without the propeller inserted. But the propeller should control the rate of expansion, slowing it down, making it less irreversible; we expect that it will lower ΔS_{univ}. Yet we know that $\Delta S_{\text{univ}} \geq 0$, with $\Delta S_{\text{univ}} = 0$ being the limit of a reversible process. Setting $\Delta S_{\text{univ}} = 0$, we see that the maximum work that we could possibly extract from the process is the negative of the change in free energy;

$$W_{\text{propeller(max)}} = -\Delta A = 1.57\text{kJ}.$$

This is an example showing the practical use of the Helmholtz free energy. It is for this reason that it was given the symbol A, standing for *Arbeit*, which is German for *work*.
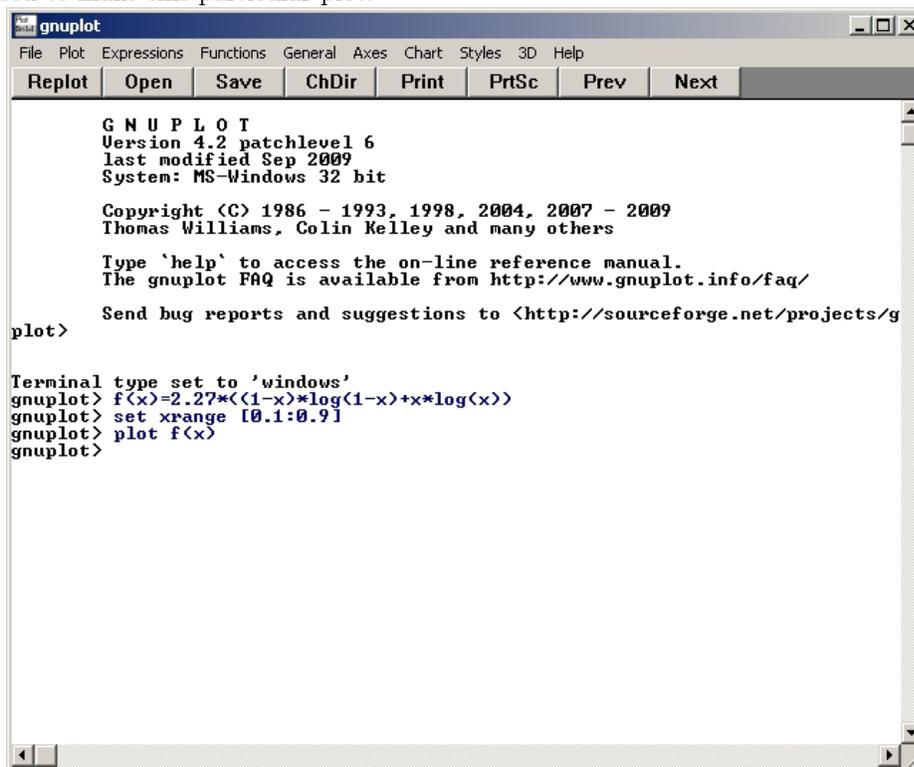
In summary, for a process taking place at constant T, for which no work is extracted, the Helmholtz free energy goes to a minimum as the entropy of the universe goes to a maximum, such that

$$\Delta A = -T\Delta S_{\text{univ.}}.$$

On the other hand, the maximum work that could be extracted were one so inclined is given by,

$$W_{\max} = -\Delta A.$$

*Here I am using GNUPLOT, a free plotting program. If you would like to use this, just go to the following website, http://www.gnuplot.info/, and follow the download instructions. Below is a screen-shot showing the commands that I used to make this particular plot:

2 Gibbs's Free Energy G

Not all spontaneous processes take place in situations where $W = 0$. In particular, many processes take place at constant pressure. For processes taking place

at constant T and P (and so many processes do!) we can show that the change in the Gibbs free energy,

$$G = H - TS.$$

is inversely proportional to the entropy change of the universe. The proof is as follows.

We have already shown that the change in enthalpy is equal to the heat for a process that takes place at constant pressure,

$$\Delta H = Q; \text{ (constant P)}.$$

(See Lecture 4 for proof.) At constant P and T it follows that,

$$\begin{aligned} \Delta G &= \Delta H - \Delta(TS) \\ &= Q - T\Delta S. \end{aligned}$$

Since the surroundings always take on heat reversibly, and $Q_{\mathrm{surr}} = -Q$, it follows that $Q = -T\Delta S_{\mathrm{surr}}$. Substituting for Q in the expression above, we have

$$\begin{aligned} \Delta G &= -T\Delta S_{\mathrm{surr}} - T\Delta S \\ &= -T\left(\Delta S_{\mathrm{surr}} + \Delta S\right) \\ &= -T\Delta S_{\mathrm{univ}}.(\text{constant. } T, P) \end{aligned}$$

As long as $T \neq 0$, when ΔS_{univ} increases, ΔG decreases. When S_{univ} reaches a maximum, G reaches a minimum. Thus we can restate the criteria for equilibrium as follows: *A system at constant T and P will evolve to minimize its Gibbs free energy.*

Can ΔG be used to determine maximum work, in a manner similar to ΔA? Indeed it can. Following the same procedure as for A, we find that for a process occurring spontaneously at constant T and P, the maximum work that can

$$W_{\mathrm{max(other)}} = -\Delta G$$

The only difference here is that, in contrast to ΔA, the maximum work calculated from ΔG isn't all of the the work, since pressure-volume work is included as part of the system's energy when we swap H for U. We call it the "other" maximum work, that would be in addition to pressure-volume work. In many cases, we are indeed interested in other means of extracting work, such as through electrical or thermal mechanisms, and often we are not interested in harnessing the additional work that might come from expansion of our system against the ambient atmosphere.

3 Generalized Free Energies (T not constant)

There are many cases where the spontaneous processes include heating or cooling, and once again we are interested in finding the maximum work that could be extracted by some reversible process (if one were clever enough to invent

one, and careful enough to build a machine to carry it out.) One way is find the maximum work in such a case is to imagine placing a Carnot engine between system and surroundings, taking the system to be one heat reservoir, and the surroundings to be the other heat reservoir, and extracting a little bit of work in every cycle as the system cools down or warms up. The work extracted by following a reversible path between the initial and final states will always be the maximum work. But another way that achieves the same end is to introduce a "generalized" free energy, either

$$\mathcal{A} = U - T_{\mathrm{surr}}S$$

for processes that take place at constant volume, or

$$\mathcal{G} = H - T_{\mathrm{surr}}S$$

for processes that take place at constant pressure. As you can see, the only difference between these and the free energies introduced above is that the temperature T has been replaced by the temperature of the surroundings T_{surr}. With this simple substitution, it follows that $\mathcal{A}$ evolves to a minimum as S_{univ} evolves to a maximum when $W = 0$, and that maximum work that could be extracted for the same change in state, were one so inclined, is given by

$$W_{\mathrm{max}} = -\Delta \mathcal{A} = T_{\mathrm{surr}}\Delta S_{\mathrm{univ}}$$

Similarly, for processes occurring at constant pressure,

$$W_{\mathrm{max(other)}} = -\Delta \mathcal{G} = T_{\mathrm{surr}}\Delta S_{\mathrm{univ}}$$

The proofs are straight forward, following the procedures outlined above, but simply substituting T_{surr} for T.

Let us work out a simple example. Consider 100 g of hot coffee at an initial temperature $T_1 = 373$ K (boiling hot) in contact with the surroundings at 294 K (70 degrees F), that spontaneously cools to $T_2 = 294$ K at constant pressure. However, let us pretend that we don't actually know what the final temperature of the coffee will be, and look for the value of T_2 that minimizes the generalized Gibb's free energy. Take the specific heat of the coffee to be $\overline{C_p} = 4.184$ J/gK and assume that it is nearly constant over this temperature range. To find $\mathcal{G}$, we need ΔS and ΔH. Using the first law, $dH = TdS + VdP$, at constant pressure we have

$$dS = \frac{dH}{T} = C_p\frac{dT}{T}$$

Integrating both sides gives

$$
\begin{aligned}
\Delta S &= C_p \ln\left(\frac{T_2}{T_1}\right) \\
&= 418.4 \ln\left(\frac{T_2}{373}\right)
\end{aligned}
$$

On the other hand,

$$\begin{aligned} \Delta H &= C_p(T_2 - T_1) \\ &= 418.4(T_2 - 373) \end{aligned}$$

Putting these together, we have

$$\begin{aligned} \Delta\mathcal{G} &= \Delta H - T_{\text{surr}}\Delta S \\ &= 418.4\left[(T_2 - 373) - 294\ln\left(\frac{T_2}{373}\right)\right] \end{aligned}$$

Below I show a graph of $\Delta\mathcal{G}$ (the y axis) versus T_2 (the x axis). I divided by 1000, so the y axis is in units of kJ. The initial state is located at $x = 373$ (the initial temperature) and $y = 0$ ($\mathcal{G} = 0$). The minimum is marked on the graph at $x = 294$ (the temperature that maximizes the entropy of the universe is the same as the temperature of the surroundings, as we had anticipated). You can see by inspecting the graph that $W_{\text{max(other)}} = -\Delta\mathcal{G} = 3.77$ kJ.
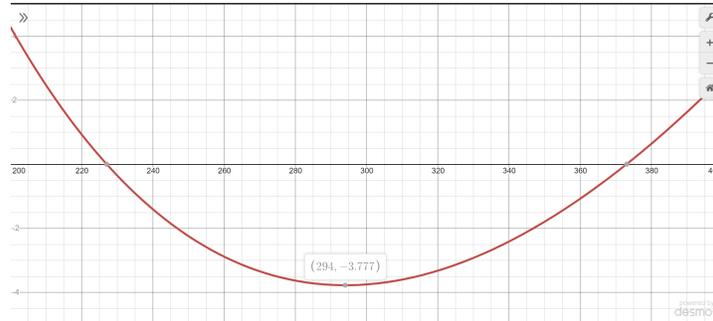
You can see that the generalized free energy can be used for two purposes. First, the principle that it goes to a minimum as the entropy of the universe can be used to find the final state. In this case, we find that the final temperature is 294 K. Second, amount that the free energy decreases between initial and final states is the maximum work (the reversible work) that we could expect to extract from the cooling process. This is the "free energy" that is always there for the taking, for any process that occurs in nature, if we are clever enough to figure out how to harvest it.