I.   Last time we discussed Hydrogen fuel cells and the ways in which G helps us to understand them. As a precursor we looked at measuring enthalpies with a coffee cup calorimeter.

We also tried to setup a discussion of equilibrium in a new context. The old context was that of fixing the extensive parameter, say U, V and N. In that previous context we found that equilibrium was characterized by the maximum entropy configuration of the system.

Let's begin anew to study equilibrium in the context of a constant temperature environment.

II. In a constant temperature environment we cannot think of the system as having a definite energy: after all it is exchanging heat with its environment.

If allow ourselves to think of our small system and its environment as a single large system, we can apply the previous insights:
For the large system we know that entropy is maximized.
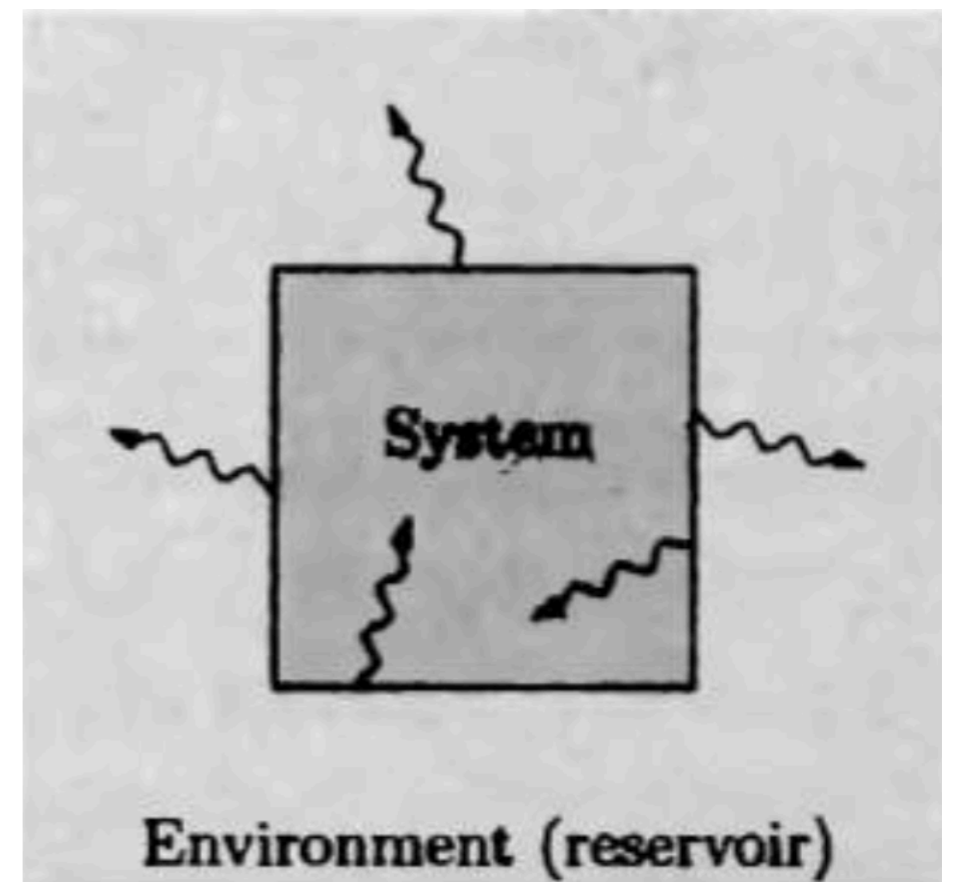The total entropy is
$$S_{\text{total}} = S + S_R.$$
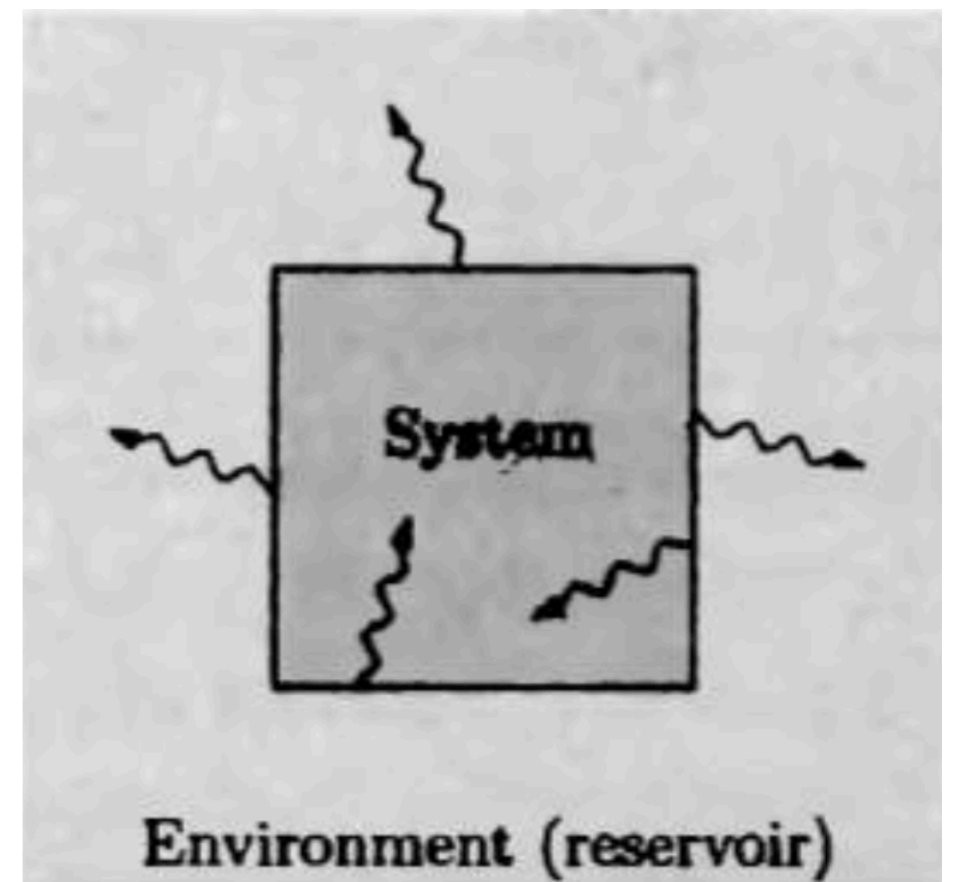Let's consider a small change
$$dS_{\text{total}} = dS + dS_R.$$
Let's restrict consideration to exchanges of heat, but not volume or particles.
Recall: $dS = \dfrac{1}{T}dU + \dfrac{P}{T}dV - \dfrac{\mu}{T}dN.$

System

Environment (reservoir)

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Then $dS_{total} = dS + dS_R = dS + \dfrac{1}{T}dU_R$

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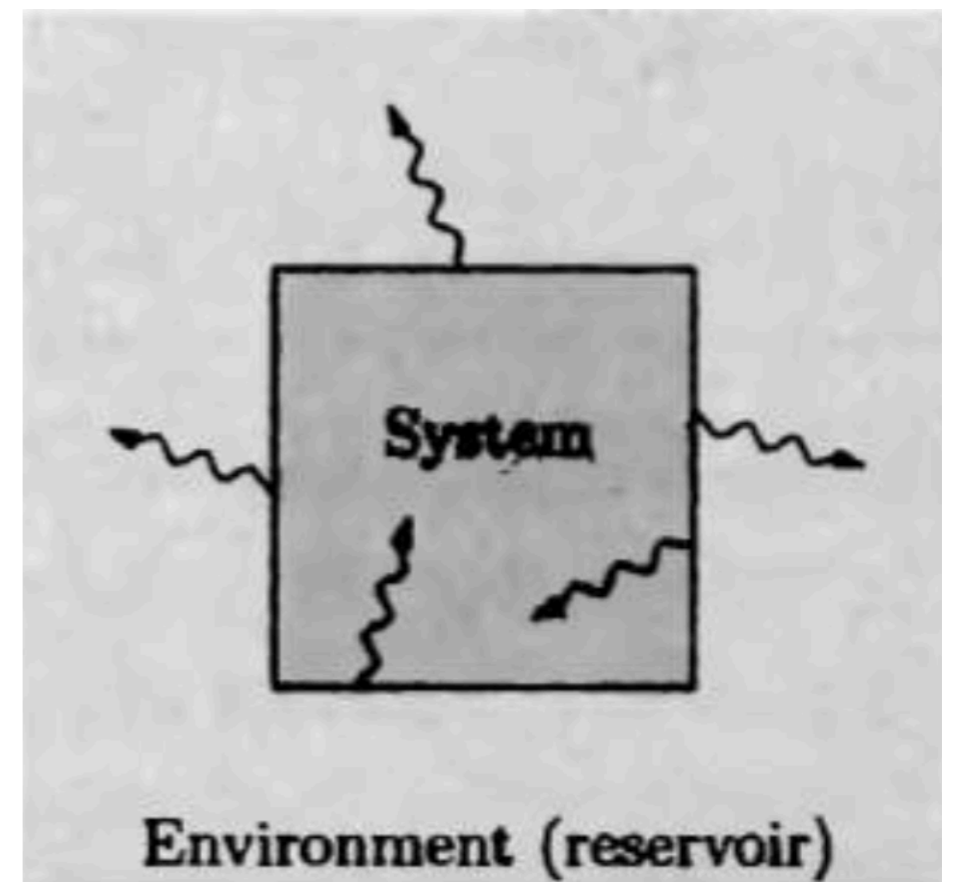

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Notice that when $dS_{total} = 0$ we also have $dF = 0$ and we can even see that this is a minimum of the free energy. This characterizes constant temperature equilibrium.

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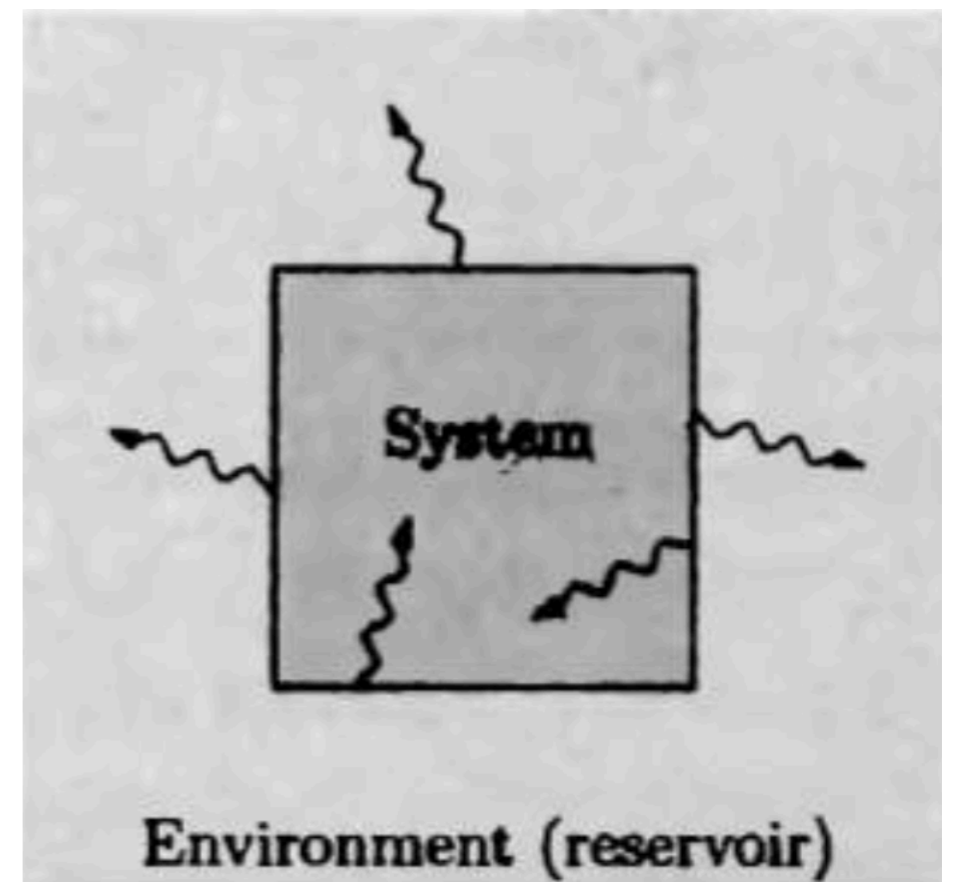$= dS - \dfrac{1}{T}dU = -\dfrac{1}{T}(dU - TdS) = -\dfrac{1}{T}dF.$

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Recall that Nathalie showed that $\Delta F \leq W$. If no work is done on the system, then F can only decrease.


Environment (reservoir)

II. We could also look for equilibrium conditions in a constant temperature and constant pressure environment.
Notice that this means the system can exchange volume with its environment.

$$dS_{total} = dS - \frac{1}{T}dU - \frac{P}{T}dV = -\frac{1}{T}dG$$

Entropy maximization becomes Gibbs free energy minimization. It turns out that the Gibbs free energy perspective is productive for looking at phase transitions. Let's try to establish this quantitatively.

Environment (reservoir)
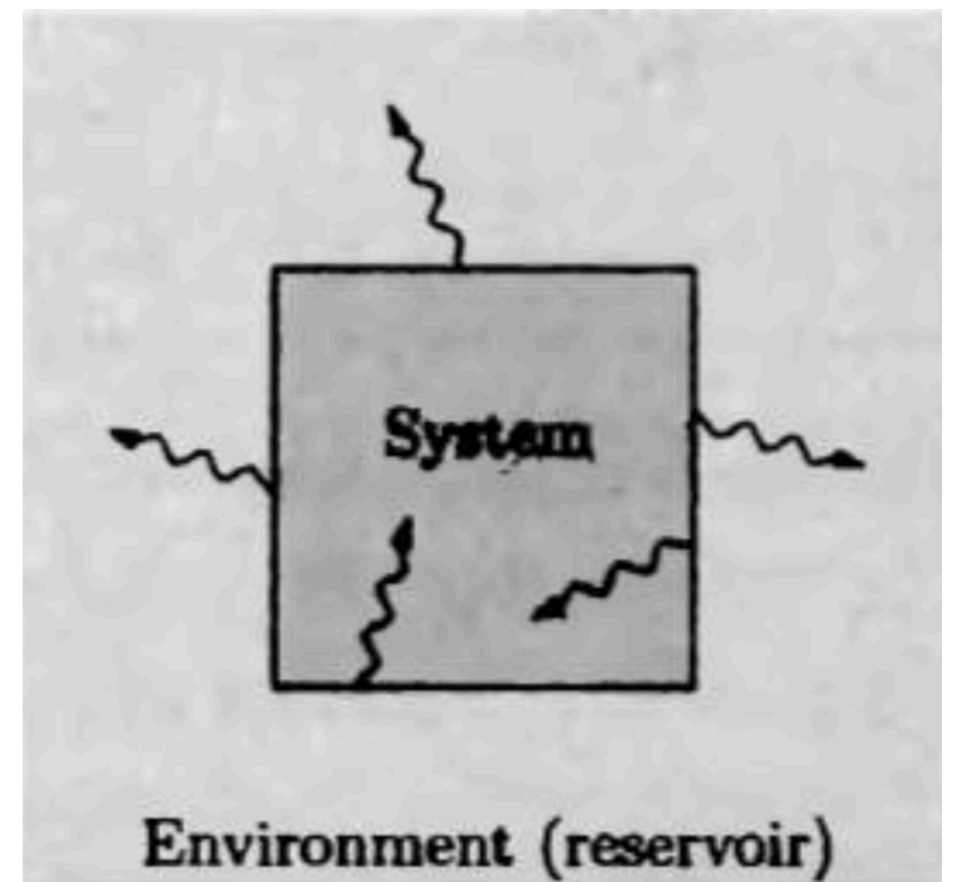
III. Euler has a wonderful way of thinking about extensive systems.

Returning our roots, consider the internal energy, which is an extensive variable. On the other hand, it is born a function of $S, V,$ and N. Then $U = U(S, V, N)$. Then

$$2U(S, V, N) = U(2S, 2V, 2N)$$

or more generally

$$\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N).$$

Let's apply the chain rule, in particular taking the derivative of both sides with respect to λ:

$$U(S, V, N) = \frac{d}{d\lambda} U(\lambda S, \lambda V, \lambda N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} S + \left(\frac{\partial U}{\partial V}\right)_{S,N} V + \left(\frac{\partial U}{\partial N}\right)_{S,V} N$$

$$= TS - PV + \mu N. \quad (dU = TdS - PdV + \mu dN)$$

Then: $F = U - TS = -PV + \mu N$; $G = U - TS + PV = \mu N$.

What's G a function of? $G = G(P, T, N) = \mu(P, T)N$