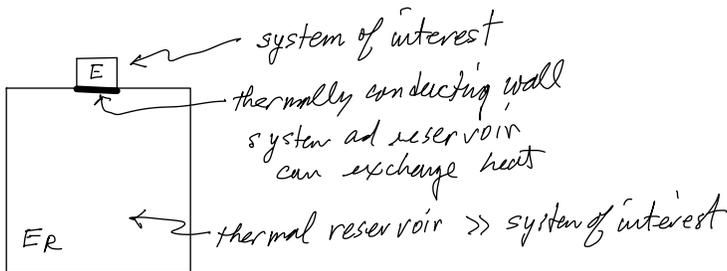


Unit 1-6: Reservoirs and the Extremum Principles for Free Energies

We have seen that when a constraint is relaxed, equilibrium is reached by maximizing the entropy S , or by minimizing the energy E , depending on whether one is using the entropy or the energy formulation of thermodynamics. Here we want to see what happens if we are using a formulation based on one of the free energies introduced in the previous section.

The Thermal Reservoir

First we introduce the concept of a *thermal reservoir*. We imagine that our system of interest is in contact with a much larger system we call the reservoir. The system of interest and the reservoir are in contact via a thermally conducting wall, so that they can exchange heat with each other, but not volume or number of particles. The combined system of interest plus the reservoir are thermally insulated from the rest of the universe.



Suppose we add heat $dQ = TdS$ to the reservoir. The change in the reservoir's temperature T_R will be,

$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R} \right)_{V_R N_R} dS = \left(\frac{\partial^2 E_R}{\partial S_R^2} \right)_{V_R N_R} dS \quad \text{since} \quad T_R = \left(\frac{\partial E_R}{\partial S_R} \right)_{V_R N_R} \quad (1.6.1)$$

Since both E_R and S_R are extensive variables, they scale proportional to the number of particles in the reservoir N_R . So,

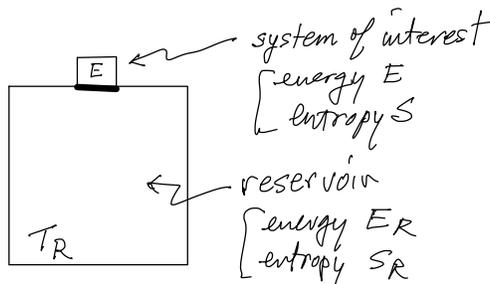
$$\left. \begin{aligned} \left(\frac{\partial^2 E_R}{\partial S_R^2} \right)_{V_R N_R} &\sim \frac{N_R}{N_R^2} \sim \frac{1}{N_R} \rightarrow 0 \\ \Rightarrow \Delta T_R &\rightarrow 0 \end{aligned} \right\} \quad \text{for an infinitely large reservoir.} \quad (1.6.2)$$

Since the system of interest is of size $\sim N$, the amount of heat it can exchange with the reservoir is of size $\sim N$ and so $dS \sim N$, and therefore $\Delta T_R \sim N/N_R \rightarrow 0$ as the reservoir grows much larger than the system of interest.

Formally, a thermal reservoir is a system so large that its temperature does not change when it exchanges heat with the much smaller system of interest. The temperature of the reservoir always stays fixed at T_R .

Minimization Principle for the Helmholtz Free Energy $A(T, V, N)$

Consider a system of interest in contact with a thermal reservoir. Only energy can be exchanged between the system of interest (henceforth just called the "system") and the reservoir. The volume and number of particles stay fixed. The temperature of the reservoir T_R stays constant by definition. All external walls are thermally insulating.



Let us use the entropy formulation to describe the combined system plus reservoir. The total energy of the combined system plus reservoir is conserved, so $E^{\text{tot}} = E_R + E$ stays constant. Let us imagine that the system is in equilibrium with the thermal reservoir, and then let some internal constraint in the system be relaxed. As the combined system comes to its new equilibrium, the total entropy S^{tot} gets maximized. Now since entropy is additive,

$$S^{\text{tot}} = S_R(E_R) + S(E) = S_R(E^{\text{tot}} - E) + S(E) \quad (1.6.3)$$

Note, since the system and reservoir cannot exchange volume or number of particles, N and V of the system, and N_R and V_R of the reservoir, stay fixed and so for convenience we will write S just as a function of energy E , as above.

Since $E \ll E^{\text{tot}}$ ($E \ll E_R \leq E^{\text{tot}}$, since the system is much smaller than the reservoir), we can expand,

$$S^{\text{tot}} \simeq S_R(E^{\text{tot}}) - \left(\frac{\partial S_R}{\partial E_R} \right) E + S(E) = S_R(E^{\text{tot}}) - \frac{E}{T_R} + S(E) \quad \text{since} \quad \left(\frac{\partial S_R}{\partial E_R} \right) = \frac{1}{T_R} \quad (1.6.4)$$

$$= S_R(E^{\text{tot}}) - \frac{(E - T_R S)}{T_R} = S_R(E^{\text{tot}}) - \frac{(E - TS)}{T} \quad (1.6.5)$$

$$= S_R(E^{\text{tot}}) - \frac{A}{T} \quad \text{since } T_R = T \text{ as system and reservoir are in thermal equilibrium.} \quad (1.6.6)$$

The term $S_R(E^{\text{tot}})$ is a constant since E^{tot} stays fixed. $A = E - T_R S = A - TS$ is the Helmholtz free energy of the system. We can set $T_R = T$ because we know that when the system is in equilibrium with the reservoir the temperatures of system and reservoir must be equal.

Since we know that S^{tot} becomes maximized as the system comes into equilibrium, we thus see from Eq. (1.6.6) that the Helmholtz free energy of the system A must be *minimized*.

The equilibrium state of a system in contact with a thermal reservoir will be the one that *minimizes* its Helmholtz free energy $A(T, V, N)$.

Minimization Principle for the Gibbs Free energy $G(T, p, N)$

Now consider a system that is in contact with a much larger system (the reservoir) via a thermally conducting wall that is also moveable. So the system and the reservoir can now exchange both energy and volume. This is now a thermal *and* pressure reservoir.

When the reservoir is much larger than the volume of the system, then any exchange of volume dV between system and reservoir results in a pressure change in the reservoir,

$$\Delta p_R = \left(\frac{\partial p_R}{\partial V_R} \right) dV = \left(\frac{\partial^2 E_R}{\partial V_R^2} \right) dV \sim \frac{N}{N_R} \quad (1.6.7)$$

Since $dV < V \sim N$ and $(\partial^2 E_R / \partial V_R^2) \sim N_R / N_R^2 \sim 1/N_R$. Thus when the reservoir is much larger than the system, $N/N_R \rightarrow 0$ and $\Delta p_R \rightarrow 0$.

A pressure reservoir is a system so large compared to the system that its pressure p_R always stays constant no matter how much volume it exchanges with the system.

For the combined system plus thermal and pressure reservoir, the total energy and total volume stay constant,

$$E^{\text{tot}} = E_R + E \quad V^{\text{tot}} = V_R + V \quad (1.6.8)$$

When the system is equilibrium with the reservoir we will have $T = T_R$ and $p = p_R$.

Now let some internal constraint in the system be relaxed. As the combined system plus reservoir comes to its new

equilibrium, the total entropy will be maximized. We can write,

$$S^{\text{tot}} = S_R(E_R, V_R) + S(E, V) = S_R(E^{\text{tot}} - E, V^{\text{tot}} - V) + S(E, V) \quad (1.6.9)$$

$$\simeq S_R(E^{\text{tot}}, V^{\text{tot}}) - \left(\frac{\partial S_R}{\partial E_R} \right) E - \left(\frac{\partial S_R}{\partial V_R} \right) V + S(E, V) \quad (1.6.10)$$

$$= S_R(E^{\text{tot}}, V^{\text{tot}}) - \frac{E}{T_R} - \frac{p_R}{T_R} V + S(E, V) \quad (1.6.11)$$

$$= S_R(E^{\text{tot}}, V^{\text{tot}}) - \frac{(E + pV - TS)}{T} \quad \text{since } T_R = T \text{ and } p_R = p \quad (1.6.12)$$

$$= S_R(E^{\text{tot}}, V^{\text{tot}}) - \frac{G}{T} \quad (1.6.13)$$

where $G(T, p, N) = E - TS + pV$ is the Gibbs free energy of the system. Thus we conclude,

The equilibrium state of a system in contact with a thermal and pressure reservoir will be the one that *minimizes* its Gibbs free energy $G(T, p, N)$.

Similarly, the equilibrium state of a system in contact with a pressure reservoir will be the one that minimizes its enthalpy $H(S, p, N)$.

And the equilibrium state of a system in contact with a thermal and particle reservoir (a particle reservoir can exchange particles with the system, but is so large that its chemical potential μ_R stays constant) will be the one that minimizes its grand potential $\Phi(T, V, \mu)$.

Note, the above arguments about maximizing S^{tot} of the system plus reservoir led to conclusions that could alternatively be stated as:

For a thermal reservoir we should *maximize* $-A/T$.

For a thermal and pressure reservoir we should *maximize* $-G/T$.

For a thermal and particle reservoir we should *maximize* $-\Phi/T$.

Recall from the discussion at the end of the previous section, if we took Legendre transforms of S rather than E , we get:

Transform S from E to $1/T$ gives $-A/T$.

Transform S from E to $1/T$ and from V to p/T gives $-G/T$.

Transform S from E to $1/T$ and from N to $-\mu/T$ give $-\Phi/T$.

So we can view these in a unified way. Equilibrium will be determined as follows:

Just like we minimize E in the energy formulation, so we minimize its Legendre transforms A , G , and Φ .

Just like we maximize S in the entropy formulation, so we maximize its Legendre transforms, $-A/T$, $-G/T$, and $-\Phi/T$.