Helmholtz free energy

F is the total energy needed to create the system, minus the heat we can get "*for free*" from the environment at temperature T. If we annihilate the system, we can't recover all its U as work, because we have to dispose its entropy at a non-zero T by dumping some heat into the environment.
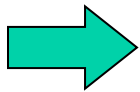
Let us do the Legendre transformation to exclude S:

$$U(S,V) \rightarrow U(T,V) - TS \qquad \boxed{F \equiv U - TS}$$

$$\boxed{dF(T,V,N) = -SdT - PdV + \mu dN}$$

The natural variables for F are *T, V, N*:

$$dF(T,V,N) = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$\boxed{\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \qquad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -P \qquad \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu}$$
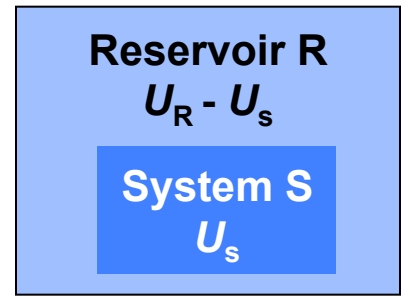
$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial U}{\partial V}\right)_{T,N} + T\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

The first term – the "energy" pressure – is dominant in most solids, the second term – the "entropy" pressure – is dominant in gases. (For an ideal gas, U does not depend on V, and only the second term survives).

The Minimum Free Energy Principle (V, T = const)

$$U = U_R + U_s, \left(U_R \; ? \; U_s \right)$$

$$N, V \text{ of both are fixed}$$

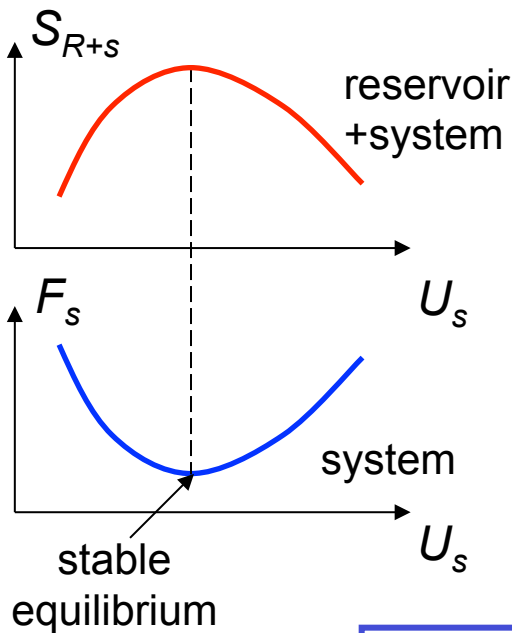The total energy of the combined system is to be shared between the reservoir and the system. Sharing is controlled by the maximum entropy principle

Reservoir R
$U_R - U_s$

System S
U_s

$$S_{R+s}\left(U_R, U_s \right) = S_R \left(U - U_s \right) + S_s \left(U_s \right) \rightarrow \max$$

system's parameters only

$$S_{R+s}\left(U, U_s \right) = S_R \left(U \right) + \left(\frac{\partial S_R}{\partial U} \right)\left(-U_s \right) + S_s \left(U_s \right) = S_R \left(U \right) - \left[\frac{U_s}{T} - S_s \right] = S_R \left(U \right) - \frac{F_s}{T}$$

loss in S_R due to transferring U_s to the system

gain in S_s due to transferring U_s to the system

S_{R+s}

reservoir +system

U_s

F_s

system

U_s

stable equilibrium

$$dS_{R+s}\left(U, U_s \right) = dS_s - \frac{dU_s}{T} =$$

$$-\frac{1}{T}\left[dU_s - TdS_s \right]$$

$$dS_{R+s} = -\frac{dF_s}{T}$$

$$F_s = \min$$

The maximum entropy principle of an isolated system is transformed into a minimum Helmholtz free energy principle for a system in thermal contact with the bath

In general, if we consider processes with "other" work:

$$dF = -SdT - PdV + \delta W_{other}$$

For the processes at T = const (in thermal equilibrium with a large reservoir):

$$(dF)_T = (-PdV + \delta W_{other})_T$$

The *total* work performed on a system at T=const in a *reversible* process is equal to the change in the Helmholtz free energy of the system. In other words, for the T=const processes, the Helmholtz free energy gives all the reversible work.

Problem: Consider a cylinder separated into two parts by an adiabatic piston. Compartments *a* and *b* each contains one mole of a monatomic ideal gas, and their initial volumes are V_{ai}=10l and V_{bi}=1l, respectively. The cylinder, whose walls allow heat transfer only, is immersed in a large bath at 0°C. The piston is now moving reversibly so that the final volumes are V_{af}=6l and V_{bi}=5l. How much work is delivered by (or to) the system?

U_A, V_A, S_A U_B, V_B, S_B
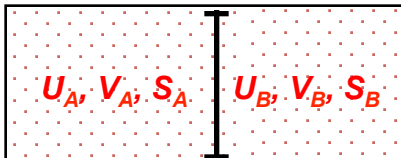
The process is isothermal : $\quad (dF)_T = (-PdV)_T$

The work delivered to the system: $\quad \delta W = \delta W_a + \delta W_b = \int\limits_{V_{ai}}^{V_{af}} dF_a + \int\limits_{V_{bi}}^{V_{bf}} dF_b$

$$F = U - TS = \frac{3}{2}RT - \left(\frac{3}{2}RT\ln\frac{T}{T_0} + RT\ln\frac{V}{V_0} + Tf(N,m)\right)$$

$$\delta W = -RT\ln\frac{V_{af}}{V_{ai}} - RT\ln\frac{V_{bf}}{V_{bi}} = -2.5\cdot10^3 \text{ J}$$

Gibbs free energy

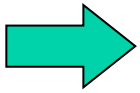Let us do the Legendre transformation to eliminate S and V:

$$U(S,V) \rightarrow U(T,P) - TS + PV$$

$$G \equiv U - TS + PV$$

The natural variables for G are T, P, N:

$$\boxed{dG(T,P,N) = -SdT + VdP + \mu dN}$$

$$dG(T,P,N) = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \qquad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \qquad \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu}$$

Gibbs Free Energy and Chemical Potential

$$G = G(T,P,N) \quad \& \quad \text{extensive:}$$

$$bG(T,P,N) = G(T,P,bN)$$

$$\boxed{G = N\mu}$$

This gives us a new interpretation of the chemical potential: at least for the systems with only one type of particles, *the chemical potential is just the Gibbs free energy per particle.*

If we add one particle to a system, holding T and P fixed, the Gibbs free energy of the system will increase by μ. By adding more particles, we do not change the value of μ since we do not change the particle density.

Note that U, H, and F, whose differentials also have the term μdN, depend on N *non-linearly*, because in the processes with the independent variables (S,V,N), (S,P,N), and (V,T,N), $\mu = \mu(N)$ might vary with N.

Pr.5.9. Sketch a qualitatively accurate graph of *G* vs. *T* for a pure substance as it changes from solid to liquid to gas at fixed pressure.

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$$

The slope of the graph *G(T)* at fixed *P* should be -*S*. Thus, the slope is always negative, and becomes steeper as T and S increases. When a substance undergoes a phase transition, its entropy increases abruptly, so the slope of *G(T)* is discontinuous at the transition.
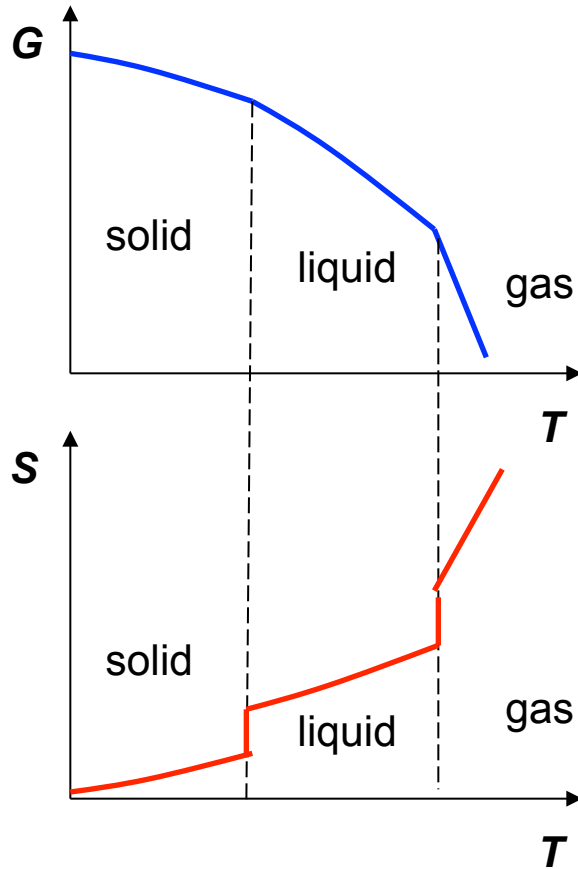
The Minimum Free Energy Principle (*P,T* = const)

$$S_{R+s}\left(U_R, U_s\right) = S_R\left(U - U_s\right) + S_s\left(U_s\right) \rightarrow \max$$

$$dS_{R+s}\left(U, U_s\right) = dS_s - \frac{dU_s}{T} - \frac{P}{V}dV_s = -\frac{1}{T}\left[dU_s - TdS_s + PdV_s\right] = -\frac{dG_s}{T}$$

Under these conditions (fixed *P, T*, and *N*), the maximum entropy principle of an isolated system is transformed into a minimum Gibbs free energy principle for a system in the thermal contact + mechanical equilibrium with the reservoir.

$$\left(dG\right)_{T,P,N} \leq 0 \quad \Longrightarrow \quad \boxed{G = \min}$$

Thus, we can enforce the maximum entropy principle by simply minimizing the Gibbs free energy of the system without having to know anything about the reservoir except that it maintains a fixed *T and P*!

Let's consider the processes at P = const and T = const in general, including the processes with "other" work:

$$\delta W = -PdV + \delta W_{other}$$

$$dG = d(U - TS + PV)_{T,P} = (\delta Q - PdV + \delta W_{other})_{T,P} - TdS + PdV$$
$$= (\delta Q)_{T,P} + (\delta W_{other})_{T,P} - TdS = (\delta W_{other})_{T,P}$$

The "other" work performed on a system at T = const and P = const in a *reversible* process is equal to the change in the Gibbs free energy of the system.

In other words, the Gibbs free energy gives all the reversible work except the PV work. If the mechanical work is the only kind of work performed by a system, the Gibbs free energy is conserved: $dG = 0$.

The Gibbs free energy is particularly useful when we consider the chemical reactions at constant P and T, but the volume changes as the reaction proceeds. ΔG associated with a chemical reaction is a useful indicator of weather the reaction will proceed spontaneously. Since the change in G is equal to the maximum "useful" work which can be accomplished by the reaction, then a *negative ΔG* indicates that *the reaction can happen spontaneously.* On the other hand, if ΔG is positive, we need to supply the minimum "other" work $\delta W_{other} = \Delta G$ to make the reaction go.

Maxwell relations

The mixed derivatives of TPs are equal

$$\text{e.g. } dU = TdS - PdV + \mu dN$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_{S,N} = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right) = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

$$\text{similarly, } \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N}, \quad \left(\frac{\partial P}{\partial N}\right)_{S,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{S,N}$$