

## 2.7: Thermodynamic Potentials

Thermodynamic systems may do work on their environments. Under certain constraints, the work done may be bounded from above by the change in an appropriately defined *thermodynamic potential*.

### Energy $E$

Suppose we wish to create a thermodynamic system from scratch. Let's imagine that we create it from scratch in a thermally insulated box of volume  $V$ . The work we must do to assemble the system is then  $\mathcal{W} = E$ . After we bring all the constituent particles together, pulling them in from infinity (say), the system will have total energy  $E$ . After we finish, the system may not be in thermal equilibrium. Spontaneous processes will then occur so as to maximize the system's entropy, but the internal energy remains at  $E$ .

We have, from the First Law,  $dE = \delta Q - \delta W$  and combining this with the Second Law in the form  $\delta Q \leq T dS$  yields

$$dE \leq T dS - \delta W \quad (2.7.1)$$

Rearranging terms, we have  $\delta W \leq T dS - dE$ . Hence, the work done by a thermodynamic system under conditions of constant entropy is bounded above by  $-dE$ , and the maximum  $\delta W$  is achieved for a reversible process. It is sometimes useful to define the quantity

$$\delta W_{free} = \delta W - p dV, \quad (2.7.2)$$

which is the differential work done by the system other than that required to change its volume. Then we have

$$\delta W_{free} \leq T dS - p dV - dE, \quad (2.7.3)$$

and we conclude for systems at fixed  $(S, V)$  that  $\delta W_{free} \leq -dE$ .

In equilibrium, the equality in Equation [dEqn] holds, and for single component systems where  $\delta W = p dV - \mu dN$  we have  $E = E(S, V, N)$  with

$$T = \left( \frac{\partial E}{\partial S} \right)_{V, N}, \quad -p = \left( \frac{\partial E}{\partial V} \right)_{S, N}, \quad \mu = \left( \frac{\partial E}{\partial N} \right)_{S, V}. \quad (2.7.4)$$

These expressions are easily generalized to multicomponent systems, magnetic systems,

Now consider a single component system at fixed  $(S, V, N)$ . We conclude that  $dE \leq 0$ , which says that spontaneous processes in a system with  $dS = dV = dN = 0$  always lead to a reduction in the internal energy  $E$ . Therefore, *spontaneous processes drive the internal energy  $E$  to a minimum in systems at fixed  $(S, V, N)$ .*

### Helmholtz free energy $F$

Suppose that when we spontaneously create our system while it is in constant contact with a thermal reservoir at temperature  $T$ . Then as we create our system, it will absorb heat from the reservoir. Therefore, we don't have to supply the full internal energy  $E$ , but rather only  $E - Q$ , since the system receives heat energy  $Q$  from the reservoir. In other words, we must perform work  $\mathcal{W} = E - TS$  to create our system, if it is constantly in equilibrium at temperature  $T$ . The quantity  $E - TS$  is known as the *Helmholtz free energy*,  $F$ , which is related to the energy  $E$  by a *Legendre transformation*,

$$F = E - TS. \quad (2.7.5)$$

The general properties of Legendre transformations are discussed in Appendix II, §16.

Again invoking the Second Law, we have

$$dF \leq -S dT - \delta W. \quad (2.7.6)$$

Rearranging terms, we have  $\delta W \leq -S dT - dF$ , which says that the work done by a thermodynamic system under conditions of constant temperature is bounded above by  $-dF$ , and the maximum  $\delta W$  is achieved for a reversible process. We also have the general result

$$\mathcal{W}_{free} \leq -S dT - p dV - dF, \quad (2.7.7)$$

and we conclude, for systems at fixed  $(T, V)$ , that  $\mathcal{W}_{free} \leq -dF$ .

Under equilibrium conditions, the equality in Equation [dFeqn] holds, and for single component systems where  $\mathcal{W} = p dV - \mu dN$  we have  $dF = -S dT - p dV + \mu dN$ . This says that  $F = F(T, V, N)$  with

$$-S = \left( \frac{\partial F}{\partial T} \right)_{V,N}, \quad -p = \left( \frac{\partial F}{\partial V} \right)_{T,N}, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}. \quad (2.7.8)$$

For spontaneous processes,  $dF \leq -S dT - p dV + \mu dN$  says that *spontaneous processes drive the Helmholtz free energy  $F$  to a minimum in systems at fixed  $(T, V, N)$ .*

## Enthalpy $\mathcal{H}$

Suppose that when we spontaneously create our system while it is thermally insulated, but in constant mechanical contact with a 'volume bath' at pressure  $p$ . For example, we could create our system inside a thermally insulated chamber with one movable wall where the external pressure is fixed at  $p$ . Thus, when creating the system, in addition to the system's internal energy  $E$ , we must also perform work  $pV$  in order to make room for it. In other words, we must perform work  $\mathcal{W} = E + pV$ . The quantity  $E + pV$  is known as the *enthalpy*,  $\mathcal{H}$ . (We use the calligraphic font for  $\mathcal{H}$  for enthalpy to avoid confusing it with magnetic field,  $H$ .) The enthalpy is obtained from the energy via a different Legendre transformation than that used to obtain the Helmholtz free energy  $F$ ,

$$\mathcal{H} = E + pV. \quad (2.7.9)$$

Again invoking the Second Law, we have

$$d\mathcal{H} \leq T dS - \mathcal{W} + p dV + V dp, \quad (2.7.10)$$

hence with  $\mathcal{W}_{free} = \mathcal{W} - p dV$ , we have in general

$$\mathcal{W}_{free} \leq T dS + V dp - d\mathcal{H}, \quad (2.7.11)$$

and we conclude, for systems at fixed  $(S, p)$ , that  $\mathcal{W}_{free} \leq -d\mathcal{H}$ .

In equilibrium, for single component systems,

$$d\mathcal{H} = T dS + V dp + \mu dN, \quad (2.7.12)$$

which says  $\mathcal{H} = \mathcal{H}(S, p, N)$ , with

$$T = \left( \frac{\partial \mathcal{H}}{\partial S} \right)_{p,N}, \quad V = \left( \frac{\partial \mathcal{H}}{\partial p} \right)_{S,N}, \quad \mu = \left( \frac{\partial \mathcal{H}}{\partial N} \right)_{S,p}. \quad (2.7.13)$$

For spontaneous processes,  $d\mathcal{H} \leq T dS + V dp + \mu dN$ , which says that *spontaneous processes drive the enthalpy  $\mathcal{H}$  to a minimum in systems at fixed  $(S, p, N)$ .*

## Gibbs free energy $G$

If we create a thermodynamic system at conditions of constant temperature  $T$  and constant pressure  $p$ , then it absorbs heat energy  $Q = TS$  from the reservoir and we must expend work energy  $pV$  in order to make room for it. Thus, the total amount of work we must do in assembling our system is  $\mathcal{W} = E - TS + pV$ . This is the *Gibbs free energy*,  $G$ . The Gibbs free energy is obtained from  $E$  after two Legendre transformations,

$$G = E - TS + pV \quad (2.7.14)$$

Note that  $G = F + pV = \mathcal{H} - TS$ . The Second Law says that

$$dG \leq -S dT + V dp + p dV - \mathcal{W}, \quad (2.7.15)$$

which we may rearrange as  $\mathcal{W}_{free} \leq -S dT + V dp - dG$ . Accordingly, we conclude, for systems at fixed  $(T, p)$ , that  $\mathcal{W}_{free} \leq -dG$ .

For equilibrium one-component systems, the differential of  $G$  is

$$dG = -S dT + V dp + \mu dN , \quad (2.7.16)$$

therefore  $G = G(T, p, N)$ , with

$$-S = \left( \frac{\partial G}{\partial T} \right)_{p,N} , \quad V = \left( \frac{\partial G}{\partial p} \right)_{T,N} , \quad \mu = \left( \frac{\partial G}{\partial N} \right)_{T,p} . \quad (2.7.17)$$

Recall that Euler's theorem for single component systems requires  $E = TS - pV + \mu N$  which says  $G = \mu N$ . Thus, the chemical potential  $\mu$  is the Gibbs free energy per particle. For spontaneous processes,  $dG \leq -S dT + V dp + \mu dN$ , hence *spontaneous processes drive the Gibbs free energy  $G$  to a minimum in systems at fixed  $(T, p, N)$ .*

## Grand potential $\Omega$

The grand potential, sometimes called the Landau free energy, is defined by

$$\Omega = E - TS - \mu N . \quad (2.7.18)$$

Under equilibrium conditions, its differential is

$$d\Omega = -S dT - p dV - N d\mu , \quad (2.7.19)$$

hence

$$-S = \left( \frac{\partial \Omega}{\partial T} \right)_{V,\mu} , \quad -p = \left( \frac{\partial \Omega}{\partial V} \right)_{T,\mu} , \quad -N = \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} . \quad (2.7.20)$$

Again invoking Equation [ETS], we find  $\Omega = -pV$ , which says that the pressure is the negative of the grand potential per unit volume.

The Second Law tells us

$$d\Omega \leq -S dT - p dV - \mu dN - N d\mu , \quad (2.7.21)$$

hence

$$\widetilde{\mathcal{W}}_{free} \equiv \mathcal{W}_{free} + \mu dN \leq -S dT - p dV - N d\mu - d\Omega . \quad (2.7.22)$$

We conclude, for systems at fixed  $(T, V, \mu)$ , that  $\widetilde{\mathcal{W}}_{free} \leq -d\Omega$ .

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