3.23 Overview of thermodynamic potentials

Following the second law, the driving force for any change of state is the maximization of the total entropy. But depending on the type of contact of the system different sets of parameters control the experiment. Each change within a pair of parameters *coordinate* ⇔ *force* needs a Legendre transformation to get the proper thermodynamic potential (state function). We will repeat and summarize most aspects when discussing the Gibbs potential as the most relevant thermodynamic potential to describe chemical reactions:

$$\begin{aligned} G &= H - TS = F + pV = U + pV - TS \\ dG &= d\left(U + pV - TS\right) \\ dG - Vdp + SdT &= dU + pdV - TdS \leq 0 \quad \Rightarrow \quad (dG)_{p,T} \leq 0 \\ dG &= \mu dN + Vdp - SdT \end{aligned} \tag{3.58}$$

The four thermodynamic potentials (state functions) discussed here have in common that the particle number, resp. the mole number N is a coordinate. So the Gibbs potential G is twice the Legendre transformed of the inner energy U and is a function of the natural coordinates $G(N, p, T)$.
In summary:

State function	Natural Variable	Spont. Process	Equilibrium
S	U, V	$(dS)_{U,V} > 0$	S = Max.
U	S, V	$(dU)_{S,V} < 0$	U = Min.
H	S, p	$(dH)_{S,p} < 0$	H = Min.
F	T, V	$(dF)_{T,V} < 0$	F = Min.
G	T, p	$(dG)_{T,p} < 0$	G = Min.

We will briefly discuss the meaning of $(dG)_{T,p}$:

$$\begin{aligned} (dG)_{T,p} &= d\left(U + pV - TS\right)_{T,p} \\ &= \left(\delta q + \delta w_{el} + \delta w_{chem} + \delta w_{expansion} + \delta w_{...} + pdV + Vdp - TdS - SdT\right)_{T,p} \\ &= \left(\delta w_{el} + \delta w_{chem} + \delta w_{...}\right) \quad \text{since} \quad \delta q = TdS \quad \text{and} \quad \delta w_{expansion} = -pdV \end{aligned} \tag{3.59}$$

So $(\Delta G)_{T,p}$ is the maximum non-expansion work done by the system and it is the right quantity to describe chemical and electrochemical equilibrium.
Correspondingly we find for $(dF)_{T,V}$: Maximum work (including expansion work) done by the system.