Thermodynamic potentials [tln4]

- All thermodynamic potentials of a system are related to each other via *Legendre transform*. Therefore, every thermodynamic potential has its distinct set of *natural independent variables*.
- All thermodynamic properties of a system can be inferred from any of the thermodynamic potentials. Any thermodynamic potential thus yields a *complete macroscopic description* of a thermodynamic system.
- Any quantity U, E, A, G, Ω which is not expressed as a function of its natural independent variables is not a thermodynamic potential and thus contains only partial thermodynamic information on the system.
- In *thermodynamics*, we determine thermodynamic potentials from *empirical macroscopic information* such as equations of state and response functions.
- In *statistical mechanics*, we determine thermodynamic potentials via partition functions from the *microscopic specification* (Hamiltonian) of the thermodynamic system.
- Any spontaneous i.e. irreversible process at constant values of the natural independent variables is accompanied by a *decrease* of the associated thermodynamic potential.
- The equilibrium state for fixed values of a set of natural independent variables is the state where the associated thermodynamic potential is a *minimum*.
- In the total differentials below, "=" holds for *reversible* processes and "<" for *irreversible* processes.

Internal energy: (set $X \equiv V, M$ and $Y \equiv -p, H$)

$$U(S,X,N) = TS + YX + \mu N, \qquad dU = \; TdS + YdX + \mu dN.$$

Enthalpy:

$$E(S,Y,N) = U - YX = TS + \mu N, \qquad dE = \; TdS - XdY + \mu dN.$$

Helmholtz free energy:

$$A(T,X,N) = U - TS = YX + \mu N, \qquad dA = -SdT + YdX + \mu dN.$$

Gibbs free energy:

$$G(T,Y,N) = U - TS - YX = \mu N, \qquad dG = -SdT - XdY + \mu dN.$$

Grand potential:

$$\Omega(T,X,\mu) = U - TS - \mu N = YX, \qquad d\Omega = -SdT + YdX - Nd\mu.$$