1.3 Thermodynamic potentials and Legendre Transformation

The power of thermodynamics results from the existence of thermodynamic potentials which allow to quantify all relevant changes quantitatively and provide many useful relations between thermodynamic parameters.
The inner energy $U(V, N, S)$ is the thermodynamic potential for the coordinates V, N, and S, i.e.

$$dU = \frac{\partial U}{\partial N}dN + \frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial S}dS := \mu dN - pdV + TdS \tag{1.21}$$

is a total differential.
The free energy F is defined by the Legendre transformation

$$F(V, N, T) = U(V, N, T) - S(V, N, T)T \quad . \tag{1.22}$$

We have

$$dF = dU - SdT - TdS = \mu dN - pdV + TdS - SdT - TdS = \mu dN - pdV - SdT \quad , \tag{1.23}$$

so $F(V, N, T)$ is the thermodynamic potential for the coordinates V, N, and T.
The enthalpy H is defined by the Legendre transformation

$$H(p, N, S) = U(p, N, S) + V(p, N, S)p \quad . \tag{1.24}$$

We have

$$dH = dU + pdV + Vdp = \mu dN - pdV + TdS + pdV + Vdp = \mu dN + Vdp + TdS \quad , \tag{1.25}$$

so $H(p, N, S)$ is the thermodynamic potential for the coordinates p, N, and S.
The Gibbs potential (free enthalpy) G is defined by a second Legendre transformation

$$G(p, N, T) = F(p, N, T) + V(p, N, T)p \quad , \tag{1.26}$$

leading to

$$dG = dF + pdV + Vdp = \mu dN - pdV - SdT + pdV + Vdp = +Vdp - SdT + \mu dN \quad . \tag{1.27}$$

Since thermodynamic potentials are extensive parameters, i.e. they scale with the size of the system, $G \propto N$, and using Eq. (1.27) we finally get

$$G(p, N, T) = \mu(p, N, T)N \quad . \tag{1.28}$$

The Gibbs potential is the most important thermodynamic potential in solid state physics and chemistry because typically in an open system pressure and temperature are defined by the external and e.g. in a mixture of solid and liquid at thermodynamic equilibrium automatically pressure and chemical potential stay constant within the system.