Maxwell Relations

Since internal energy U is a state function, its Legendre transform, the thermodynamics potentials, is also a state function. One of the characteristic of state function is that their differential is an exact differential.

For constant particle $dN = 0$, we write those the state functions differential as

$$\begin{aligned}
dU(S,V) &= \left.\frac{\partial U}{\partial S}\right|_V dS + \left.\frac{\partial U}{\partial V}\right|_S dV = T\,dS - P\,dV \\
dF(T,V) &= \left.\frac{\partial F}{\partial T}\right|_V dT + \left.\frac{\partial F}{\partial V}\right|_T dV = -S\,dT - P\,dV \\
dG(T,P) &= \left.\frac{\partial G}{\partial T}\right|_P dT + \left.\frac{\partial G}{\partial P}\right|_T dP = -S\,dT + V\,dP \\
dH(S,P) &= \left.\frac{\partial H}{\partial S}\right|_P dS + \left.\frac{\partial H}{\partial P}\right|_S dP = T\,dS + V\,dP
\end{aligned}$$

Them being exact would imply

$$\begin{aligned}
\left.\frac{\partial T}{\partial V}\right|_S &= -\left.\frac{\partial P}{\partial S}\right|_V & \qquad \left.\frac{\partial S}{\partial V}\right|_T &= \left.\frac{\partial P}{\partial T}\right|_V \\
\left.\frac{\partial S}{\partial P}\right|_T &= -\left.\frac{\partial V}{\partial T}\right|_P & \qquad \left.\frac{\partial T}{\partial P}\right|_S &= \left.\frac{\partial V}{\partial S}\right|_P
\end{aligned}$$

Fundamental Set

Definition. Three fundamental set are: heat capacity at constant volume C_V, adiabatic compressibility κ_S, and adiabatic thermal expansion α_S; which are defined as follows.

$$C_V = \left.\frac{\partial Q}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V, \quad \kappa_S = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_S, \quad \alpha_s = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_S$$

Primary Set

Definition. Primary set also contain three parametes: heat capacity at constant pressure C_P, isothermal compressibility κ_T, and isobaric thermal expansion α_S; which are defined as follows.

$$C_P = \left.\frac{\partial Q}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P, \quad \kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_P, \quad \alpha_s = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$$