Appendix A: Various Thermodynamic Functions have different Natural Independent Variables

Key idea: Natural Independent Variables of a thermodynamic function

- When developing thermodynamics from zeroth, first, second laws, we encountered T, U, S, V, p, N.
  Even if we consider molar quantities (one mole), we still have T, U, S, V, p.
- We just saw an example

$$\boxed{dS = \frac{1}{T}dU + \frac{p}{T}dV}$$

The entropy S has U and V as its natural independent variables

Why? If we know $S(U,V)$, then the other two variables follow immediately by

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \quad \text{and} \quad p = T\left(\frac{\partial S}{\partial V}\right)_U}$$

Thus, $S(U,V)$ OR $S(U,V,N)$ gives all information of a system.

In contrast, if we know $S(T,p)$, recall Eq. (*) on p. II-⑮,

$$dS = \frac{C_p(T)}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p(T)}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

which are quite far from giving V, U!

- Similarly, $\underbrace{H = U + pV}_{H(S,p)}$ widely used in chemistry (constant p processes)

  $\underbrace{F = U - TS}_{F(T,V)}$ widely used in statistical mechanics [canonical ensemble]

  $\underbrace{G}_{G(T,p)} = U - TS + pV = H - TS = F + pV$ widely used in chemistry

  and $U(S,V)$

Ex: If we know $U(T,V)$, what does $\left(\frac{\partial U}{\partial T}\right)_V$ give?