

Quiz problem 1: Construct a thermodynamic potential with natural variables temperature T pressure p , and particle number N : Gibbs free energy $G(T, p, N)$

1. Derive the thermodynamic identity for G .

Solution:

Recall that,

$$dU = TdS - pdV + \mu dN \quad (1)$$

where,

$$\left. \frac{\partial U}{\partial S} \right|_{V,N} = T \quad \left. \frac{\partial U}{\partial V} \right|_{S,N} = -p \quad \left. \frac{\partial U}{\partial N} \right|_{S,V} = \mu \quad (2)$$

We want to transform $U(S, V, N)$ to $G(T, p, N)$, so let's define

$$G \equiv U - S \left. \frac{\partial U}{\partial S} \right|_V + p \left. \frac{\partial U}{\partial V} \right|_{S,N} \quad (3)$$

$$\equiv U - ST + pV \quad (4)$$

So,

$$\boxed{G = U - ST + pV} \quad (5)$$

2. Calculate all Maxwell relations that can be derived from G .

Solution:

The total differential of G is,

$$dG = \left. \frac{\partial G}{\partial T} \right|_{p,N} dT + \left. \frac{\partial G}{\partial p} \right|_{T,N} dp + \left. \frac{\partial G}{\partial N} \right|_{T,p} dN \quad (6)$$

$$= \left. \frac{\partial U}{\partial T} \right|_{p,N} dT + \left. \frac{\partial U}{\partial p} \right|_{T,N} dp + \left. \frac{\partial U}{\partial N} \right|_{T,p} dN + \left. \frac{\partial [ST + pV]}{\partial T} \right|_{p,N} dT + \left. \frac{\partial [ST + pV]}{\partial p} \right|_{T,N} dp + \left. \frac{\partial [ST + pV]}{\partial N} \right|_{T,p} dN \quad (7)$$

$$= -SdT + Vdp + \mu dN \quad (8)$$

3. Show that for extensive systems the chemical potential is given by:

$$\mu = \frac{G}{N} \quad (9)$$

Solution:

Recall the Euler equation, for an extensive system

$$U = TS - pV + \mu N \quad (10)$$

We can use this in our definition of G ,

$$G = [TS - pV + \mu N] - ST + pV \quad (11)$$

So for a extensive system,

$$\mu = \frac{G}{N} \quad (12)$$