

**Problem 6.1.**

We know that the free energy  $F(T, V, N)$  of a thermodynamic system is extensive. Show that

$$N \left( \frac{\partial F}{\partial N} \right)_{T, V} + V \left( \frac{\partial F}{\partial V} \right)_{T, N} = Nf = F$$

with  $f$  the free energy density expressed in suitable variables. Given this result, from the differential properties of  $F(T, V, N)$ , show that

$$\Phi = N\mu$$

with  $\Phi$  the Gibbs potential defined as  $\Phi = F + PV$ . In the above expression,  $\mu$  is the chemical potential properly defined in terms of  $F(T, V, N)$ .

$$dU = TdS - PdV + \mu dN \quad / \quad F = U - TS$$

$$dF = -SdT - PdV + \mu dN$$

$$dF = \left( \frac{\partial F}{\partial T} \right)_{V, N} dT + \left( \frac{\partial F}{\partial V} \right)_{T, N} dV + \left( \frac{\partial F}{\partial N} \right)_{T, V} dN$$

Comparando se obtiene

$$\left( \frac{\partial F}{\partial T} \right)_{V, N} = -S \quad ; \quad \left( \frac{\partial F}{\partial V} \right)_{T, N} = -P \quad , \quad \left( \frac{\partial F}{\partial N} \right)_{T, V} = \mu \quad (*)$$

del calculo previo

$$N \left( \frac{\partial F}{\partial N} \right)_{T, V} = \underbrace{N \left( \frac{\partial F}{\partial N} \right)_{T, V}}_{\mu} + \underbrace{V \left( \frac{\partial F}{\partial V} \right)_{T, N}}_{-P}$$

$$Nf - V \left( \frac{\partial F}{\partial V} \right)_T + V \left( \frac{\partial F}{\partial V} \right)_T = Nf \quad // \quad \text{demostrado.}$$

pero si usamos

$$N \left( \frac{\partial F}{\partial N} \right)_{T, V} + V \left( \frac{\partial F}{\partial V} \right)_{T, N} = Nf = F$$

$$N\mu - VP = F$$

$$N\mu = F + PV$$

$$N\mu = G$$

// demostrado

$$\rightarrow dU = Tds - PdV + \mu dN$$

$$U = Ts - PV + \mu N$$

$$H = Ts + \mu N$$

$$F = -PV + \mu N$$

$$G = \mu N \quad //$$

$$(H = U + PV)$$

$$(F = U - Ts)$$

$$(G = H - Ts)$$