

Chemical Potential and Gibbs Distribution

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- Chemical Potential, $\mu(\tau, V, N)$
 - Given a reservoir, R with fundamental temperature τ , and two systems in contact, S_1 and S_2 , with τ, V_1, N_1 and τ, V_2, N_2 , respectively
 - R is in thermal equilibrium with S_1 and S_2
 - R is in mechanical equilibrium with S_1 and S_2
 - S_1 is in mechanical equilibrium with S_2 , which means V_1 and V_2 are constant
 - N_1 and N_2 can change, but $N_1 + N_2 = N$ is constant
 - We find that the partial of F with respect to N plays an important role in this situation
 - We find that the chemical potential can be represented as:

$$\mu(\tau, V, N) \equiv \left(\frac{\partial F(\tau, V, N)}{\partial N} \right)_{\tau, V}$$

- * In chemical equilibrium, $\mu_1 = \mu_2$
 - We can find that, away from equilibrium:

$$dF_{S_1+S_2} = (\mu_1 - \mu_2)dN_1$$

- This implies that particles flow from greater energy to lower energy (this makes sense, as they would want to settle at minimal potential)
- The chemical potential must be defined for all particle species:

$$\mu_i = \left(\frac{\partial F(\tau, V, N_1, N_2, N_3)}{\partial N_i} \right)_{\tau \forall N_{k \neq i}}$$

- The chemical potential of an ideal gas then becomes:

$$F = -\tau N \left(\ln \left(\frac{n_Q}{n} \right) + 1 \right)$$

* Note: we also know $\frac{n_Q}{n} = \frac{N}{V}$

– By taking the partial with respect to N , we get:

$$\mu = -\tau \ln \left(\frac{n_Q}{n} \right)$$

– From this, we can tell:

* $\mu < 0$ because $n \ll n_Q$ in classical regime

* if n increases, then μ increases

– Using $F = U - \tau\sigma$, we can determine internal and external chemical potentials as:

$$\mu_{ext} = \left(\frac{\partial F_{ext}}{\partial N} \right)_{\tau, V} = \left(\frac{\partial U_{ext}}{\partial N} \right)_{\tau, V} = \frac{U_{ext}}{N}$$

$$\mu_{int} = \left(\frac{\partial F_{int}}{\partial N} \right)_{\tau, V}$$

• We know that in chemical equilibrium, $\mu_{1|total} = \mu_{2|total}$, or, more generally:

$$\mu_{1|int} + \frac{U_{1|ext}}{N_1} = \mu_{2|int} + \frac{U_{2|ext}}{N_2}$$