

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:

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

- Thermodynamic Relations

$$\text{dependent thermodynamic functions} \rightarrow \begin{cases} \sigma &= \sigma(\overbrace{U, V, N}^{\text{nat. ind. vars}}) \\ U &= U(\sigma, V, N) \\ F &= F(\tau, V, N) \end{cases}$$

The differentials for these may be written as:

$$d\sigma = \overbrace{\left(\frac{\partial \sigma}{\partial U} \right)_{V, N}}^{\frac{1}{\tau}} dU + \overbrace{\left(\frac{\partial \sigma}{\partial V} \right)_{U, N}}^{\frac{P}{\tau}} dV + \overbrace{\left(\frac{\partial \sigma}{\partial N} \right)_{U, V}}^{-\frac{\mu}{\tau}} dN$$

$$dU = \overbrace{\left(\frac{\partial U}{\partial \sigma} \right)_{V, N}}^{\tau} d\sigma + \overbrace{\left(\frac{\partial U}{\partial V} \right)_{\sigma, N}}^P dV + \overbrace{\left(\frac{\partial U}{\partial N} \right)_{\sigma, V}}^{\mu} dN$$

$$dF = \underbrace{\left(\frac{\partial F}{\partial \tau} \right)_{V, N}}_{?} d\tau + \underbrace{\left(\frac{\partial F}{\partial V} \right)_{\tau, N}}_{-P} dV + \underbrace{\left(\frac{\partial F}{\partial N} \right)_{\tau, V}}_{\mu} dN$$

- Gibbs Distribution

- Given a reservoir, R , and system, S , we find:

- * R and S are in thermal and chemical equilibrium
- * $R + S$ is closed
- * All volumes are fixed
- * $U_R + \varepsilon_S = U_o$ (constant)
- * $N_R + N = N_o$ (constant)
 - Where N is the number of particles of S , and ε_S is the energy of S in a quantum state s of particles N
- * This means:

$$g_{R+S} = g_R(N_R, U_R) \cdot \overbrace{g_S(N, \varepsilon_S)}^1$$

- * Which would then give us the probability to find S in a quantum state $S(N)$:

$$P(N, \varepsilon_S) \approx g_{R+S} = g_R(N_R, U_R)$$

- * Ultimately, we obtain the probability as:

$$P(N, \varepsilon_S) = e^{\sigma_R(N_o, U_o) + \left(-\frac{\mu}{\tau}\right)(-N) + \left(\frac{1}{\tau}\right)(-\varepsilon_S)}$$

- * ε becomes the grand canonical partition function:

$$\sum_N \sum_{S(N)} P(N, \varepsilon_S) = 1$$

$$\varepsilon(\mu, \tau, V) = \sum_N \sum_{S(N)} e^{\frac{\mu N - \varepsilon_S}{\tau}}$$

- Where N is the number of all particles, and $S(N)$ are all quantum states for a given N

$$\langle N \rangle = \sum_N \sum_{S(N)} N \cdot P(N, \varepsilon_S) = \tau \left(\frac{\partial \ln(\varepsilon)}{\partial \mu} \right)_{\tau, V}$$