From previous class:

$$\sum_{i=1}^{r} n_i \mu_{Ai} = \sum_{i=1}^{s} n_i' \mu_{Bi}$$

$$\mu_i = k_B T \ln P_i + \chi_i(T)$$

$$\chi_i \simeq -k_B T \ln\left[\frac{k_B T\, g_{i0}}{\lambda_i^3}\right] + \varepsilon_{i0}$$

$$\sum_{i=1}^{r} n_i \left[\ln \frac{[A_i]P}{\rho} - \ln\left(\frac{k_B T\, g_{A_i 0}}{\lambda_{A_i}^3}\right) + \frac{\varepsilon_{A_i 0}}{k_B T}\right]$$

$$= \sum_{i=1}^{s} n_i' \left[\ln \frac{[B_i]P}{\rho} - \ln\left(\frac{k_B T\, g_{B_i 0}}{\lambda_{B_i}^3}\right) + \frac{\varepsilon_{B_i 0}}{k_B T}\right]$$

$$\Rightarrow \frac{[A_1]^{n_1} \cdots [A_r]^{n_r}}{[B_1]^{n_1'} \cdots [B_s]^{n_s'}} = \left(\frac{P}{\rho k_B T}\right)^{\sum_i n_i' - \sum_i n_i} \frac{\prod_i \lambda_{B_i}^3 / g_{B_i 0}}{\prod_i \lambda_{A_i}^3 / g_{A_i 0}} \exp\left(\frac{\sum_i n_i' \varepsilon_{B_i 0} - \sum_i n_i \varepsilon_{A_i 0}}{k_B T}\right)$$

$$\Rightarrow \boxed{\frac{[A_1]^{n_1} \cdots [A_r]^{n_r}}{[B_1]^{n_1'} \cdots [B_s]^{n_s'}} = \left(\frac{P\,(2\pi\hbar^2)^{3/2}}{\rho\,(k_B T)^{5/2}}\right)^{\sum_i n_i' - \sum_i n_i} \frac{\prod_i g_{A_i 0}}{\prod_i g_{B_i 0}} \left(\frac{\prod_i m_{A_i}}{\prod_i m_{B_i}}\right)^{3/2} \exp\left(\frac{\sum_i n_i' \varepsilon_{B_i 0} - \sum_i n_i \varepsilon_{A_i 0}}{k_B T}\right)}$$

Thermal Ionization

Elements get ionized at high temperature (e.g. in stellar atmospheres).

$A \rightleftharpoons A^{+} + e$ where A is some element, e.g., Na, Ca, ...

$A^{+} \rightleftharpoons A^{2+} + e$

$\vdots$

$A^{(n-1)+} \rightleftharpoons A^{n+} + e$

Applying the boxed equation to the last reaction, we get,

$$\boxed{\frac{[A^{(n-1)+}]}{[A^{n+}][e]} = \frac{p\,(2\pi\hbar^2)^{3/2}}{\rho\,(k_BT)^{5/2}}\,\frac{g_{n-1}}{2g_n}\,\frac{1}{m^{3/2}}\,e^{I_n/k_BT} \text{ --- Megh Nad Saha (1921)}}$$

g_n = ground state degeneracy of A^{n+} ion

Ground state degeneracy of electron $= 2$

$I_n = \mathcal{E}_{n0} - \mathcal{E}_{n-1,0}$, $\mathcal{E}_{n0}$ = ground state energy of A^{n+} ion (non - translational)

m = mass of an electron

If the temperature is such that the highest ionized state is A^+, then,

let α = degree of ionization = fraction of ionized atoms $= \dfrac{[A^+]}{[A]+[A^+]}$

By charge neutrality, $[A^+] = [e]$

Also, $\rho = [A]+[A^+]+[e] = [A^+] + [A^+]/\alpha \;\Rightarrow\; [A^+] = \dfrac{\alpha\rho}{1+\alpha}$

$$[A] = \frac{[A^+]}{\alpha} - [A^+] \;\Rightarrow\; [A] = \frac{1-\alpha}{1+\alpha}\rho$$

From Saha's equation,

$$\frac{[A]}{[A^+][e]} = \frac{p\,(2\pi\hbar^2)^{3/2}}{\rho\,(k_BT)^{5/2}}\,\frac{g_0}{2g_1}\,\frac{1}{m^{3/2}}\,e^{I_1/k_BT}$$

$$\frac{[A]}{[A^+][e]} = \frac{\left(\frac{1-\alpha}{1+\alpha}\right)\rho}{\left(\frac{\alpha\rho}{1+\alpha}\right)^2} = \frac{1-\alpha^2}{\alpha^2\rho}$$

$$\Rightarrow \boxed{\frac{1-\alpha^2}{\alpha^2} = p\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2}\frac{1}{k_BT}\,\frac{g_0}{2g_1}\,e^{I_1/k_BT} \text{ --- Saha's Ionization formula}}$$