

From previous class:

$$\sum_{i=1}^r n_i \mu_{A_i} = \sum_{i=1}^s n'_i \mu_{B_i}$$

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

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

$$\sum_{i=1}^r n_i \left[\ln \frac{[A_i] P}{f} - \ln \left(\frac{k_B T g_{A_{i0}}}{\lambda_{A_i}^3} \right) + \frac{\epsilon_{A_{i0}}}{k_B T} \right]$$

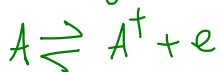
$$= \sum_{i=1}^s n'_i \left[\ln \frac{[B_i] P}{f} - \ln \left(\frac{k_B T g_{B_{i0}}}{\lambda_{B_i}^3} \right) + \frac{\epsilon_{B_{i0}}}{k_B T} \right]$$

$$\Rightarrow \frac{[A_1]^{n_1} \dots [A_r]^{n_r}}{[B_1]^{n'_1} \dots [B_s]^{n'_s}} = \left(\frac{P}{f k_B T} \right)^{\sum_i n'_i - \sum_i n_i} \frac{\prod_i \lambda_{B_i}^3 / g_{B_{i0}}}{\prod_i \lambda_{A_i}^3 / g_{A_{i0}}} \exp \left(\frac{\sum_i n'_i \epsilon_{B_{i0}} - \sum_i n_i \epsilon_{A_{i0}}}{k_B T} \right)$$

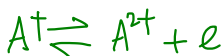
$$\Rightarrow \frac{[A_1]^{n_1} \dots [A_r]^{n_r}}{[B_1]^{n'_1} \dots [B_s]^{n'_s}} = \left(\frac{P (2\pi k_B T)^{3/2}}{f (k_B T)^{5/2}} \right)^{\sum_i n'_i - \sum_i n_i} \frac{\prod_i g_{A_{i0}}}{\prod_i g_{B_{i0}}} \left(\frac{\prod_i m_{A_i}}{\prod_i m_{B_i}} \right)^{3/2} \exp \left(\frac{\sum_i n'_i \epsilon_{B_{i0}} - \sum_i n_i \epsilon_{A_{i0}}}{k_B T} \right)$$

Thermal Ionization

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



where A is some element, e.g., Na, Ca, ...



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

$$\frac{[A^{(n-1)+}]}{[A^{n+}][e]} = \frac{P(2\pi\hbar^2)^{3/2}}{f(k_B T)^{5/2}} \frac{g_{n-1}}{2g_n} \frac{1}{m^{3/2}} e^{I_n/k_B T} \text{ --- Megh Nad Saha (1921)}$$

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

Ground state degeneracy of electron = 2

$I_n = \epsilon_{n0} - \epsilon_{n-1,0}$, ϵ_{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 = $\frac{[A^+]}{[A] + [A^+]}$

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

$$\text{Also, } f = [A] + [A^+] + [e] = [A^+] + [A^+]/\alpha \Rightarrow [A^+] = \frac{\alpha f}{1+\alpha}$$

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

From Saha's equation,

$$\frac{[A]}{[A^+][e]} = \frac{P(2\pi\hbar^2)^{3/2}}{f(k_B T)^{5/2}} \frac{g_0}{2g_1} \frac{1}{m^{3/2}} e^{I_1/k_B T}$$

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

$$\Rightarrow \frac{1-\alpha^2}{\alpha^2} = P \left(\frac{2\pi\hbar^2}{m k_B T}\right)^{3/2} \frac{1}{k_B T} \frac{g_0}{2g_1} e^{I_1/k_B T} \text{ --- Saha's Ionization formula}$$