

# VIVEKANANDA COLLEGE THAKURPUKUR KOLKATA-700063

NAAC ACCREDITED 'A' GRADE



Topic: Chemical Equilibrium and Saha's Ionization Formula  
(<https://youtu.be/JpW0EiLo9Kw>)

Course Title: Statistical Mechanics

Paper:PHY 423

Unit: 2

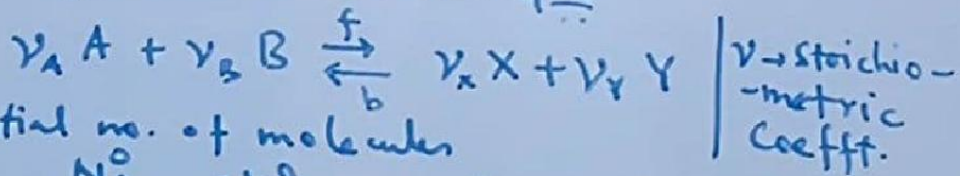
Semester: 2

Name of the Teacher:Arvind Pan

Name of the Department:Physics

# Chemical Equilibrium

$\mu \rightarrow$  determines the amount of the chemical present in chemical eqm



Initial no. of molecules

$$N_A^0 \quad N_B^0 \quad N_X^0 \quad N_Y^0$$

After  $\Delta N$  no. of chemical reaction

$$N_A = N_A^0 - \nu_A \Delta N$$

$$N_B = N_B^0 - \nu_B \Delta N$$

$$N_X = N_X^0 + \nu_X \Delta N$$

$$N_Y = N_Y^0 + \nu_Y \Delta N$$

$\Delta N > 0 \rightarrow$  forward reaction ;  $\Delta N < 0 \rightarrow$  backward  
 $\Delta G < 0$  ; At eqm  $\Delta G = 0$

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

$$G = A + PV = U - TS + PV$$

$$dG = dU - Tds - SdT + PdV + VdP$$

$$= \mu dN - SdT + VdP$$

Chemical Reaction ( $T = \text{const}, P = \text{const}$ )

$$dG = 0 = \mu dN \Rightarrow \mu dN = 0$$

$$\mu_A (N_A^0 - N_A) + \mu_B (N_B^0 - N_B) + \mu_X (N_X^0 - N_X) + \mu_Y (N_Y^0 - N_Y) = 0$$

$$\mu_A \nu_A + \mu_B \nu_B - \mu_X \nu_X - \mu_Y \nu_Y = 0$$

$$\sum_{\alpha} \mu_{\alpha} \nu_{\alpha} \geq 0$$

# SAHA'S IONIZATION FORMULA

$\lambda \rightarrow$  Thermal DeBroglie Wavelength

$$Q_1 = \frac{V}{h^3} (2\pi m kT)^{3/2} = \frac{V}{\lambda^3} = \frac{V}{\sigma}$$

Grand Partition funct.

$$Q = \sum_N z^N \frac{Q_1^N}{N!} \quad \left| \begin{array}{l} z \rightarrow \text{Fugacity} \\ = e^{\beta\mu} = e^{-\alpha} \end{array} \right.$$

$$= \sum_N (e^{\beta\mu})^N \frac{(V/\sigma)^N}{N!} = \exp\left(\frac{e^{\beta\mu} V}{\sigma}\right)$$

$$p = \ln Q = \frac{e^{\beta\mu} V}{\sigma} = \frac{pV}{kT}$$

$$p = kT \frac{e^{\beta\mu}}{\sigma} = \frac{e^{\beta\mu}}{\sigma \beta}$$

$$= n kT$$

where  $n \rightarrow$  no. density

$$n = \frac{e^{\beta\mu}}{\sigma} \times N \Rightarrow \mu = \frac{1}{\beta} \ln\left(\frac{n\sigma}{N}\right)$$

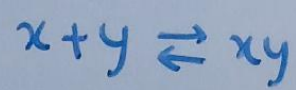
$$\sum_{\alpha} \nu_{\alpha} \mu_{\alpha} = 0 \Rightarrow \frac{1}{\beta} \sum_{\alpha} \nu_{\alpha} \ln\left(\frac{n_{\alpha} \sigma_{\alpha}}{N_{\alpha}}\right) = 0 = \ln(1)$$

$$\ln \prod_{\alpha} \left(\frac{n_{\alpha} \sigma_{\alpha}}{N_{\alpha}}\right)^{\nu_{\alpha}} = \ln(1)$$

# SAHA'S IONIZATION FORMULA

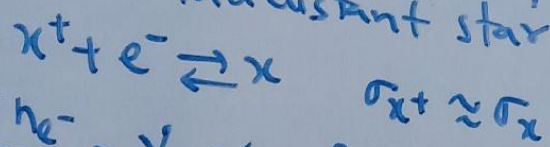
$$\prod_{\alpha} n_{\alpha}^{v_{\alpha}} = \prod_{\alpha} \left( \frac{N_{\alpha}}{\sigma_{\alpha}} \right)^{v_{\alpha}}$$

$$N_{\alpha} = N_{\alpha 0} e^{-\beta \epsilon_{\alpha}}$$



$$\frac{n_x n_y}{n_{xy}} = \left( \frac{N_x N_y}{N_{xy}} \right) \frac{\sigma_{xy}}{\sigma_x \sigma_y} e^{-\beta(\epsilon_x + \epsilon_y - \epsilon_{xy})}$$

For ionisation in a distant star



$$\frac{n_{x^+} n_{e^-}}{n_x} = \gamma \frac{\sigma_x}{\sigma_{x^+} \sigma_{e^-}} e^{-\beta \epsilon_I} \quad \left| \begin{array}{l} \epsilon_I = \text{Ionization Energy} \end{array} \right.$$

For electrical neutrality of stars  $n_{x^+} = n_{e^-}$

$$f = \frac{n_{x^+}}{n_{\text{tot}}} = \frac{n_{e^-}}{n_{\text{tot}}}$$

$$\frac{f n_{\text{tot}} \times f n_{\text{tot}}}{(1-f) n_{\text{tot}}} = \frac{\gamma}{\sigma_{e^-}} e^{-\beta \epsilon_I}$$

$$\frac{f^2}{1-f} = \frac{\gamma}{\sigma_{e^-} n_{\text{tot}}} e^{-\beta \epsilon_I}$$