VIVEKANANDA COLLEGE
THAKURPUKUR
KOLKATA-700063

NAAC ACCREDITED ‘A’ GRADE

Topic: Chemical Equilibrium and Saha’s Ionization Formula (https://youtu.be/JpWOEiLo9Kw)

Course Title: Statistical Mechanics

Paper:PHY 423

Unit: 2

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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

$$\nu_A A + \nu_B B \underset{b}{\overset{f}{\rightleftharpoons}} \nu_X X + \nu_Y Y$$

$\nu \rightarrow$ Stoichiometric Coefft.

Initial no. of molecules

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

After ΔN 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

$\Delta G \leq 0$; 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 = Const, P = Const.)

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

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

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

$$\boxed{\sum_\alpha \mu_\alpha \nu_\alpha = 0}$$

SAHA'S IONIZATION FORMULA

λ → 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.

$$\mathcal{Q} = \sum_N z^N \frac{Q_1^N}{N!}$$

z → Fugacity $= e^{\beta\mu} = e^{-\alpha}$

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

$$q = \ln \mathcal{Q} = \frac{e^{\beta\mu}V}{\sigma} = \frac{PV}{kT}$$

$$P = \frac{kTe^{\beta\mu}}{\sigma} = \frac{e^{\beta\mu}}{\sigma\beta}$$

$$= nkT$$

$$= \frac{n}{\beta}$$ where n → 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

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

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

$$x + y \rightleftarrows xy$$

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

For ionisation in a distant star

$$x^+ + e^- \rightleftarrows x \qquad \sigma_{x^+} \approx \sigma_x$$

$$\frac{n_{x^+} n_{e^-}}{n_x} = \gamma \frac{\sigma_x}{\sigma_{x^+} \sigma_{e^-}} e^{-\beta \epsilon_I} \quad \Big| \quad \epsilon_I = \text{Ionization Energy}$$

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

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

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

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