SAHA IONISATION FORMULA:

In the interior of stars, temperature are extremely high & the elements present there are mostly in atomic state. In such conditions atoms move very rapidly & undergo frequent collision. In this process they are stripped of valance e^-. This is known as thermal ionisation & is followed by e^- recapture to form neutral atoms. Saha's ionisation formula related the temperature, pressure & ionisation potential of atoms to their degree of ionisation.

It assumes following:

(1) The contribution of spin is negligible
(2) Only single ionisation occurs.
(3) Dynamical equilibrium b/w ionisation & recomb. is reached at given temp. & pressure.

Consider reaction:

no. of particles.

$$aA + bB \rightleftharpoons xX + yY$$

The reaction is taking place at constant temp. & pressure.

If N_a, N_b, N_x, N_y are corr. no. of particles taking part in reaction then Gibbs free energy will be

$$G = a\mu_a + b\mu_b + x\mu_x + y\mu_y$$

For atom of type A, $a\,dn$ is the change in no. of moles $\|^y$ $b\,dn$, $x\,dn$, $y\,dn$ is small change in B, X, Y. So change in gibbs free energy is

$$dG = -\mu_a a\,dn - \mu_b b\,dn + \mu_x x\,dn + \mu_y y\,dn$$

At equilibrium $dG = 0$

$$\Rightarrow \mu_a a\,dn + \mu_b b\,dn = \mu_x x\,dn + \mu_y y\,dn.$$

$Z = Z_t Z_i$; Z_i is partition function due to internal modes & it is a function of temp. only.

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$$Z_t = \frac{1}{N!} V^N \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2}$$

$$Z_t = \frac{1}{N!} V^N \left(\frac{2\pi m K_B T}{h^2}\right)^{3N/2}$$

$$\bar{\mu} = \frac{-1}{\beta}\frac{\partial}{\partial N}(\ln Z_N)$$

$$\ln Z_N = -\ln N! + N\ln V + \frac{3N}{2}\ln\left(\frac{2\pi K_B T m}{h^2}\right)$$

$$= -N\ln N + N + N\ln V + \frac{3}{2}N\ln\left(\frac{2\pi m K_B T}{h^2}\right)$$

$$\frac{\partial \ln Z}{\partial N} = -1 + \ln V + \frac{3}{2}\ln\left(\frac{2\pi m K_B T}{h^2}\right) - \ln N - 1$$

$$\frac{-1}{\beta}\frac{\partial \ln Z}{\partial N} = -K_B T\left[\ln \frac{V}{N} \left(\frac{2\pi m K_B T}{h^2}\right)^{3/2}\right]$$

So, $\bar{\mu} = \frac{-1}{\beta}\frac{\partial}{\partial N}\ln(Z_t)$

$$\mu = -K_B T \ln\left[\frac{V}{N}\left(\frac{2\pi m K_B T}{h^2}\right)^{3/2}\right]$$

Also,

$$G = -NK_B T \ln\left[\left(\frac{2\pi m K_B T}{h^2}\right)^{3/2}\frac{V}{N}\right]$$

$$\frac{G}{N} = \bar{\mu} = -K_B T \ln\left[\left(\frac{2\pi m K_B T}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}\right]$$

$\because$ $PV = NK_B T$

So $\frac{V}{N} = \frac{K_B T}{P}$

$$\boxed{\bar{\mu}_T = -K_B T \ln\left[\left(\frac{2\pi m K_B T}{h^2}\right)^{3/2}\cdot\frac{K_B T}{P}\right]}$$

If there are internal modes also then

$$\mu_{Total} = -K_B T \ln\left[\left(\frac{2\pi m K_B T}{h^2}\right)^{3/2}\frac{K_B T}{P}\cdot Z_i\right]$$

$m = \frac{M}{N_A}$

$$\mu_{total} = -K_B T \ln\left[\left(\frac{2\pi M K_B T}{N_A h^2}\right)^{3/2}\frac{K_B T}{P}\cdot Z_i\right]$$

For atom A

$$\mu_a = -K_B T \ln\left[\left(\frac{2\pi M_a K_B T}{N_a h^2}\right)^{3/2}\frac{K_B T}{P_a}\cdot Z_{ia}\right]$$

$M/M*$ P_s/P_e

$$\frac{M_I}{M_A} \approx 1 \qquad \frac{M_e}{N_a} \approx m_e.$$

$$\frac{P_I P_e}{P_A} = \left(\frac{2\pi m_e}{h^2}\right)^{3/2} (K_B T)^{5/2} \frac{2 g_I}{g_A} e^{-(\ )}$$

If there are N atoms out of which x atoms are ionised.

$P_I = P_e$ as system of ions & e^- will be electrically neutral.

As total pressure = sum of partial pressure

$$P = P_A + P_I + P_e$$

$$P_A = P - 2P_e$$

$$\frac{P_I P_e}{P_A} = \frac{P_e^2}{P - 2P_e} = \frac{P(P_e/P)^2}{1 - 2\left(\frac{P_e}{P}\right)} = \frac{Px^2}{1 - 2x}$$

where $x = \frac{P_e}{P}$ mole fraction of e^-

So,

$$\boxed{\frac{x^2}{1 - 2x} = \left(\frac{2\pi m_e}{h^2}\right)^{3/2} \frac{(K_B T)^{5/2}}{P} \frac{2 g_I}{g_A} e^{-(E^*/K_B T)}}$$

This eqn expresses the degree of ionisation as a function of temperature, pressure & ionisation potential of atom present in the interior of stars. This is known as Saha's Ionisation formula. It implies degree of ionisation will be more if temp. is high, or pressure & ionisation potential are low.

μ_B, μ_x, μ_y

In eqn condn

$$a\mu_a + b\mu_b = x\mu_x + y\mu_y$$

$$\ln\left(\frac{P_x^x \cdot P_y^y}{P_a^a \cdot P_b^b}\right) = \ln\left[\left[\left(\frac{2\pi}{N_A h^2}\right)^{\frac{3}{2}} (K_B T)^{5/2}\right]^{x+y-a-b} \left[\frac{M_x^x M_y^y}{M_a^a M_b^b}\right] \frac{Z_{ix}^y Z_{iy}^y}{Z_{ia}^a Z_{ib}^b}\right]$$

Reaction constant,

$$K_p = \frac{P_x^x P_y^y}{P_a^a \cdot P_b^b} = \left[\left[\left(\frac{2\pi}{N_A h^2}\right)^{3/2} (K_B T)^{5/2}\right]^{x+y-a-b} \left[\frac{M_x^x M_y^y}{M_a^b M_b^3}\right] \left(\frac{Z_{ix}^x Z_{iy}^y}{Z_{ia}^a Z_{ib}^b}\right)\right]$$

If reaction is

$$AB \rightleftharpoons A + B$$

$$K_p = \frac{P_a P_b}{P_{ab}}$$

$\frac{Z_{ia} Z_{ib}}{Z_{iab}}$ = degeneracy of the ground state.

$Z_{ia} = g_A$; $Z_{ib} = g_B$; $Z_{iab} = g_{ab} \exp(-\epsilon^*/K_B T)$

ϵ^* = Energy req. by compound AB to become A & B.

<u>Thermal Ionisation</u>

$$\overset{P_A}{A} \longrightarrow \overset{P_I}{A^+} + \overset{P_e}{e^-}$$

$$a, b, x, y = 1$$

$$K_p = \frac{P_I P_e}{P_A} (\quad)(\quad)\left(\frac{Z_I Z_e}{Z_A}\right)$$

$Z_{i,I} = g_I$ $Z_{i,A} = g_A \exp(\epsilon^*/K_B T)$

$Z_{i,e} = g_e = 2$

ϵ^* : ionisation potential.

$$\frac{P_I P_e}{P_A} = \left(\frac{2\pi}{N_A h^2}\right)^{3/2} (K_B T)^{5/2} \frac{2 g_I}{g_A} e^{-\epsilon^*/KT} \times \left(\frac{M_I M_e}{M_A}\right)^{3/2}$$