



$F = k_B T \ln Z$ free energy

$Z = \frac{Z_A^{N_A}}{N_A!} \cdot \frac{Z_B^{N_B}}{N_B!} \cdot \frac{Z_C^{N_C}}{N_C!}$ canonical partition sum

Minimize F with respect to N_A

$\frac{\partial F}{\partial N_A} \stackrel{!}{=} 0 \Rightarrow \frac{\partial}{\partial N_A} \ln Z \stackrel{!}{=} 0 \Rightarrow \frac{\partial}{\partial N_A} (N_A \ln Z_A + N_B \ln Z_B + N_C \ln Z_C - \ln N_A! - \ln N_B! - \ln N_C!)$
||
0

Stirling's formula: $\ln N! = N \ln N - N + \mathcal{O}(\ln N)$

$\frac{\partial}{\partial N} (\ln N!) \approx \frac{\partial}{\partial N} (N \ln N - N) = \ln N + N \frac{1}{N} - 1 = \ln N$

$\frac{\partial N_B}{\partial N_A} = 1 \quad \frac{\partial N_C}{\partial N_A} = -1$ (For: $\alpha A + \beta B \rightleftharpoons \gamma C \Rightarrow \frac{\partial N_B}{\partial N_A} = \frac{\beta}{\alpha}$; $\frac{\partial N_C}{\partial N_A} = -\frac{\gamma}{\alpha}$)

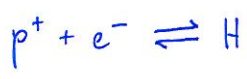
$\Rightarrow \frac{\partial}{\partial N_A} \ln Z \approx \ln Z_A + \ln Z_B - \ln Z_C - \ln N_A - \ln N_B + \ln N_C \stackrel{!}{=} 0$

$\frac{Z_A Z_B}{Z_C} = \frac{N_A N_B}{N_C}$

Law of mass action

(b) $Z_A = g_A e^{-\frac{m_A c^2}{k_B T}} \frac{V}{\lambda_A^3} \rightarrow \lambda_A = \frac{h}{\sqrt{2\pi m_A k_B T}}$ thermal wavelength

The physics of recombination



Universe is neutral: $N_e = N_p$

Number of baryons: $N_p + N_H = N_B$

$$N_H = N_B - N_e$$

$$x = \frac{N_e}{N_B}$$

$$\frac{Z_p Z_e}{Z_H} = \frac{N_p N_e}{N_H} = \frac{N_e^2}{N_B - N_e} = N_B \frac{x^2}{1-x}$$

$$\frac{g_p g_e}{g_H} V \left(\frac{\lambda_H}{\lambda_p \lambda_e} \right)^3 e^{-\frac{\Delta m}{k_B T}} = N_B \frac{x^2}{1-x}$$

$\left. \begin{matrix} \Delta m \\ (m_p + m_e - m_H)c^2 \end{matrix} \right\} E_{\text{binding}}$

$$\frac{g_p g_e}{g_H} \frac{1}{n_B} \left(\frac{2\pi k_B T}{h^2} \frac{m_p m_e}{m_H} \right)^{\frac{3}{2}} e^{-\frac{(m_p + m_e - m_H)c^2}{k_B T}} = \frac{x^2}{1-x} \quad \text{Saha's equation}$$

$$n_B = \eta n_\gamma$$

$n_\gamma \rightarrow$ photon gas number density

$$n_\gamma = 16\pi \zeta(3) \left(\frac{k_B T}{hc} \right)^3$$

$\zeta(3) \rightarrow$ Riemann zeta function at $s=3$
 $\zeta(3) \approx 1.20206$

$\hookrightarrow g_p = 2$
 $g_e = 2$
 $g_H = 1$

$\frac{m_p}{m_H} \approx 1$

$$4 \frac{1}{\eta} \frac{1}{16\pi \zeta(3)} \left(\frac{hc}{k_B T} \right)^3 \left(\frac{2\pi k_B T}{h^2} \right)^{\frac{3}{2}} m_e^{\frac{3}{2}} e^{-\frac{(m_p + m_e - m_H)c^2}{k_B T}} = \frac{x^2}{1-x}$$

$$\sqrt{\frac{\pi}{2}} \frac{1}{\eta} \frac{1}{\zeta(3)} m_e^{\frac{3}{2}} c^3 (k_B T)^{-\frac{3}{2}} e^{-\frac{(m_p + m_e - m_H)c^2}{k_B T}} = \frac{x^2}{1-x}$$

$$\underbrace{\sqrt{\frac{\pi}{2}} \frac{1}{\zeta(3)\eta} \left(\frac{m_e c^2}{k_B T} \right)^{\frac{3}{2}} e^{-\frac{(m_p + m_e - m_H)c^2}{k_B T}}}_{f(T)} = \frac{x^2}{1-x}$$

$$\frac{x^2}{1-x} = f$$

$$x = \frac{-f \pm \sqrt{f^2 + 4f}}{2} \rightarrow x = \frac{f \sqrt{1 + \frac{4}{f}} - f}{2}$$

$$x^2 = f - fx$$

$$x^2 + fx - f = 0$$