# Chemical Equilibrium

Consider a reaction

formation of neutral Hydrogen

$$A + B \longleftrightarrow C \qquad \text{for example} \qquad e + p \longleftrightarrow H$$

The energy is a function of $S$, $V$ and $N_A$, $N_B$, $N_C$

$$dU = TdS - p\,dV + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

If we are considering constant temperature and volume, we can integrate by parts defining the Free Energy, $F = U - TS$

$$dF = -S\,\cancel{dT}^{\,0} - p\,\cancel{dV}^{\,0} + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

Now at constant temperature and volume the system will evolve to minimize the free energy. If $C$ increases by the chemical reaction, $A$ and $B$ decrease accordingly

$$dN_C = -dN_A = -dN_B$$

So

Free energy decreases until it is a minimum

$$dF = (-\mu_A - \mu_B + \mu_C)\,dN_C \leq 0$$

So equilibrium is reached when

$$\boxed{-\mu_A - \mu_B + \mu_C = 0}$$

For a general reaction

$$2A + 3B \longleftrightarrow C + 2D$$

One finds similarly

$$-2\mu_A - 3\mu_B + \mu_C + 2\mu_D = 0$$

or $\sum_i \nu_i \mu_i = 0$ where $\nu_A = -2$, $\nu_B = -3$, $\nu_C = 1$, $\nu_D = 2$ are stochiometric coefficients.

## Ratio of yields in Equilibrium

Consider the reaction $e + p \leftrightarrow H$. We want to know the yields of electrons, protons, and hydrogen $n_e$, $n_p$, $n_H$. We know that the yields will adjust themselves until $\mu_p + \mu_e = \mu_H$. We need to translate this relation amongst chemical potential to a relationship amongst $n_e, n_p, n_H$. We can do this using

$$G = F + pV = \mu N$$

compute using partition functions

$$F = -kT \ln Z$$

Now

$$Z = \frac{Z_1^N}{N!} \simeq \left(\frac{eZ_1}{N}\right)^N \qquad Z_1 = \sum_s \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} e^{-\beta p^2/2m} e^{-\beta \mathcal{E}_s}$$

Sum over internal states

integral over position + momenta

So

$$G = F + pV$$

$$G = -NkT \ln\left(\frac{eZ_1}{N}\right) + NkT = -NkT \ln\left(\frac{Z_1}{N}\right)$$

Now $\mu = G/N$ which means:

$$\boxed{\mu = -kT \ln Z_1/N}$$

Or solving for $N$ we find

$$\boxed{N = e^{\mu/kT} Z_1}$$

So consider the ratio of yields

$$\frac{N_c}{N_A N_B} = e^{\beta\underbrace{(\mu_c - \mu_A - \mu_B)}} \frac{Z_{1C}}{Z_{1A} Z_{1B}}$$

But this factor is zero in equilibrium

So

$$\frac{N_c}{N_A N_B} = \frac{Z_{1C}}{Z_{1A} Z_{1B}} \equiv K_N(T)$$

this is a ratio of yields we want to know

this is called the equilibrium constant and is only a function of temperature and determined by the Z's in the process

We can see a neat relation between the equilibrium constant and the energy released during the reaction

$$-\frac{\partial}{\partial\beta}\ln K_N(\beta) = -\frac{\partial}{\partial\beta}\left(\ln Z_{1C} - \ln Z_{1A} - \ln Z_{1B}\right)$$

$$-\frac{\partial \ln K_N(\beta)}{\partial\beta} = \underbrace{\langle \varepsilon_C \rangle - \langle \varepsilon_A \rangle - \langle \varepsilon_B \rangle}$$

Change in the equilibrium constant with temperature

Difference in mean energy of reactants and products. This is the heat released per particle at constant volume

## Formation of Neutral Hydrogen

$$e + p \longleftrightarrow H$$

The density of proton nuclei ($p + H$) in the early universe is $n = (N_p + N_H)/V = 10^{20}\,m^{-3}$. Determine the relative abundance of neutral $H$ to ionized protons

$$\frac{N_p}{N_p + N_H} \quad \text{vs. Temperature}$$

We know that the universe is neutral overall $N_e = N_p$

We have

$$Z_1 = \sum_s \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3}\, e^{-\beta p^2/2m}\, e^{-\beta \varepsilon_s}$$

internal states

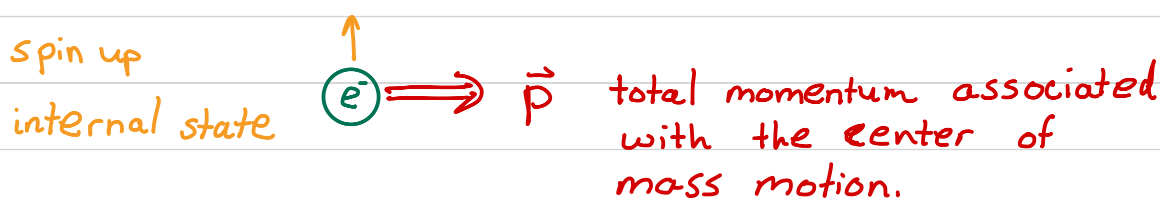
internal energy states of atom

For electrons:

$$Z_e = g_e \left( \frac{V}{\lambda_e^3} \right)$$

two internal states $g_e = 2$, for each momentum the electron can be spin up or spin down, $\varepsilon_\uparrow = \varepsilon_\downarrow = 0$ = internal energy

$Z_{1\,trans}$ with $\lambda = h/(2\pi m_e kT)^{1/2}$. $m_e$ is the electron mass.




Same for proton:

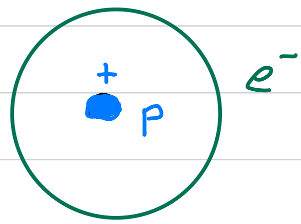
$$Z_p = g_p \left( \frac{V}{\lambda_p^3} \right)$$

$g_p = 2$ is the spin degeneracy of the proton

The $\lambda_p = h/(2\pi m_p kT)^{1/2}$. $m_p$ is the proton mass.

Finally For Hydrogen the states are labelled by the position and momentum $(\vec{r}, \vec{p})$, as well as the internal energy levels of hydrogen, as well as the spin of the electron and proton

Position + Momentum + Internal energy states of hydrogen


$$\varepsilon_n = -\frac{13.6\,eV}{n^2} \quad n = 1, 2, 3 \ldots$$

and both e and p can be spin-up or down

$$g_H = g_e g_p = 4$$

So $\quad Z_1 = Z_{1trans} Z_{1int}$

$$= \left(\frac{V}{\lambda_H^3}\right) \cdot \left(g_e g_p \sum_{n=1}^{\infty} e^{-\beta \varepsilon_n}\right)$$

we will approximate this by just including the ground state $n = 1$, $\varepsilon_1 = -13.6\,eV \equiv -R$

$$= \left(\frac{V}{\lambda_p^3}\right) g_e g_p \; e^{+\beta R}$$

The H has almost the mass of p, $\lambda_H \simeq \lambda_p$

So the ratio of yields is

$$\frac{n_H}{n_e n_p} = V \left(\frac{N_H}{N_e N_p}\right) = \frac{V Z_{1H}}{Z_{1p} \; Z_{1e}} = \frac{\cancel{\lambda_p^3} \lambda_e^3 \; \cancel{g_e} \cancel{g_p} e^{\beta R}}{\cancel{\lambda_p^3} \; \cancel{g_e} \; \cancel{g_p}}$$

$$\boxed{\frac{n_H}{n_e n_p} \simeq \lambda_e^3 e^{\beta R} \equiv K(T)}$$

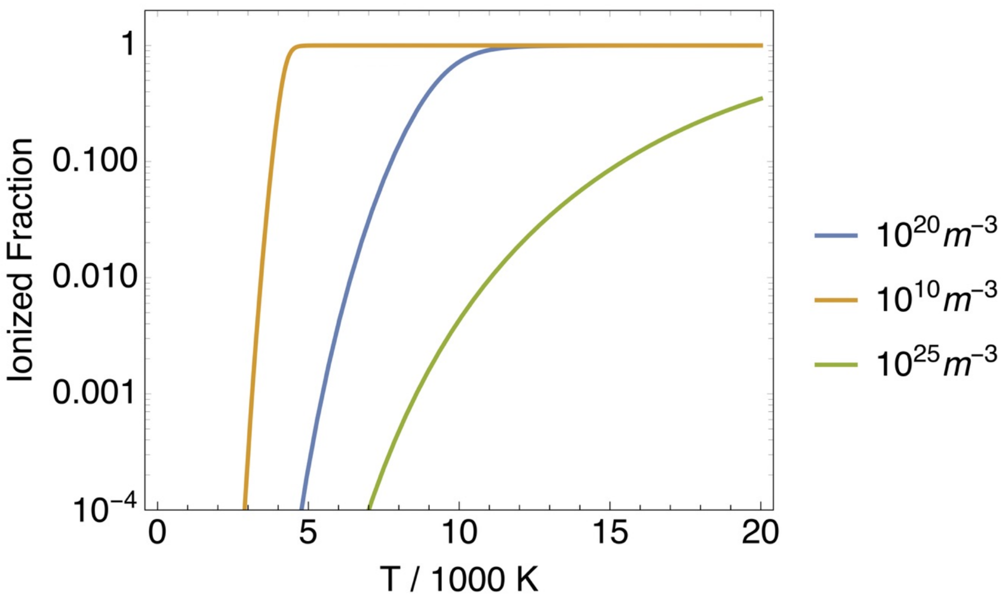
Now

(1) $n_p + n_H = 10^{20}\ 1/m^3$ $\Leftarrow$ this was the density of proton nuclei in the eary universe

(2) $n_p = n_e$ $\Leftarrow$ the universe was neutral

(3) $\dfrac{n_H}{n_e n_p} = K(T)$ $\Leftarrow$ This came from Statmech. we know $K(T) = \lambda_e^3 e^{\beta R}$

This is three equations and three unknowns, and we can solve for $n_p, n_e, n_H$. You will do this in Homework.




$$n_p + n_H \simeq 10^{20}\mathrm{m}^{-3}$$

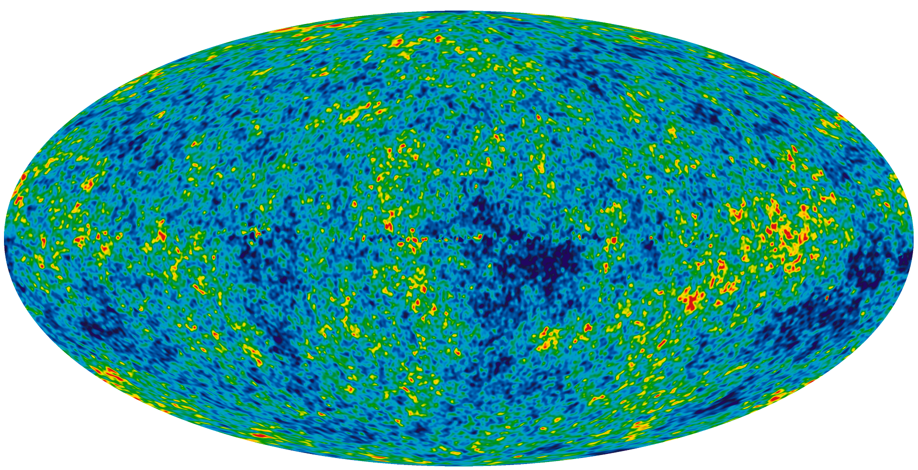
The ionized fraction is

$$\frac{n_p}{n_p + n_H}$$

So approximately at 10,000°K, we expect that the material will transition from ionized plasma at high temperature to neutral hydrogen at low temperatures. Since, light scatters strongly with charged particles (electrons), but weakly from neutral hydrogen. The light from the early universe is released at that epoch

# Cosmological Story:

Spectrum of cosmological light, reflecting a temperature of 10,000 Kelvin many years ago



13.6 Billion Years ago the universe was approximately 10,000 Kelvin

Then at this time the electrons and protons recombined, making neutral hydrogen. Since then, the light has been traveling freely, but becoming redshifted, to a lower effective temperature. We measure light at temperature of $2.7\,^o\mathrm{K}$ everywhere in the sky, reflecting $10{,}000^o\mathrm{K}$ from 13.6 billion years ago.