Gibbs

a) $G = U - TS + pV$

$$dU = TdS - pdV + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

Note

$$-d(TS) = -TdS - SdT$$

$$d(pV) = pdV + Vdp$$

So adding $dU - d(TdS) + d(pV)$ we get

$$dG = -SdT + Vdp + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

b) Then

$$U = U(S, V, N_A, N_B, N_C)$$

- Under rescaling by a factor λ

$$\lambda U(S, V, N_A, N_B, N_C) = U(\lambda S, \lambda V, \lambda N_A, \lambda N_B, \lambda N_C) \equiv U_\lambda$$

- Then differentiating w.r.t. λ we have

$$U(S, V, N_A, N_B, N_C) = \left.\frac{\partial U_\lambda}{\partial(\lambda S)}\right|_{\lambda=1} S + \left.\frac{\partial U_\lambda}{\partial(\lambda V)}\right|_{\lambda=1} V + \sum_{x=A,B,C} \left.\frac{\partial U_\lambda}{\partial(\lambda N_x)}\right|_{\lambda=1} N_x$$

So

$$\left.\frac{\partial U_\lambda}{\partial(\lambda S)}\right|_{\lambda=1} = T \qquad \left.\frac{\partial U_\lambda}{\partial(\lambda V)}\right|_{\lambda=1} = -p \qquad \left.\frac{\partial U}{\partial(\lambda N_x)}\right|_{\lambda=1} = \mu_x$$

So

$$\boxed{U = TS - pV + \mu_A N_A + \mu_B N_B + \mu_C N_C}$$

So

$$G = \mu_A N_A + \mu_B N_B + \mu_C N_C$$

c) So since at constant temperature & pressure

$$dG = \mu_A \, dN_A + \mu_B \, dN_B + \mu_C \, dN_C$$

- If the reaction progresses forward we have

$$dN_A = -1, \quad dN_B = -1, \quad dN_C = +1$$

And

$$dG = -\mu_A - \mu_B + \mu_C$$

- Since in equilibrium we have $dG = 0$ we have

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

Problem: Yields

a) So

$$Z_{tot} = \frac{Z_1^N}{N!} \simeq \left(\frac{eZ_1}{N}\right)^N$$

Then

$$F = -kT \ln Z_{tot} = -kTN \ln\left(\frac{eZ_1}{N}\right) = -kTN\left[\ln\frac{Z_1}{N} + 1\right]$$

So

$$\mu = \left(\frac{\partial F}{\partial N}\right)_T = -kT\left[\ln\left(\frac{Z_1}{N}\right) + 1\right] + kTN\frac{\partial}{\partial N}(\ln N + const)$$

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

Now

b) $Z_1 = Z_1^{trans} Z_{int}$

- $Z_1^A = V n_Q^A \cdot 1$ with $n_Q^A = \frac{(2\pi m^A k_B T)^{3/2}}{h^3}$
- $Z_1^B = V n_Q^B \cdot 1$
- $Z_1^C = V n_Q^C \cdot \sum_s e^{-\beta \varepsilon_s}$

$$Z_1^C = V n_Q^C e^{\beta \Delta}$$

Then

$$e^{\mu_A/kT} = \frac{N}{Z_1}$$

Now this yields:

$$\boxed{e^{\mu_A/kT} = \frac{N}{V n_Q^A} = \frac{n^A}{n_Q^A}}$$

Similarly

$$\boxed{\begin{aligned} e^{\mu_B/kT} &= \frac{n}{n_Q^B} \\ e^{\mu_c/kT} &= \frac{n}{n_Q^c} e^{-\beta\Delta} \end{aligned}}$$

Finally sine

$$e^{+(\mu_A+\mu_B-\mu_c)/kT} = 1 \quad \text{we have:}$$

$$\left(\frac{n^A}{n_Q^A}\right)\left(\frac{n^B}{n_Q^B}\right)\left(\frac{n_Q^c\, e^{\beta\Delta}}{n_c}\right) = 1$$

Or

$$\frac{n^A\, n^B}{n_c} = \left(\frac{n_Q^A\, n_Q^B}{n_Q^c}\right) e^{-\beta\Delta}$$

So

$$n_c \propto n^A n^B e^{\beta\Delta}$$

if the Binding energy is strong we get lots of particle C. But the yield of C is limitted by the availability of A and B.

We note $n_Q = C_0 m^{3/2}$ or $n_Q = (2\pi m kT)^{3/2}/h^3$

$\hookrightarrow C_0 = (2\pi kT)^{3/2}/h^3$

$$\frac{n_Q^A n_Q^B}{n_Q^C} = C_0 \left(\frac{m_A m_B}{m_A + m_B}\right)^{3/2}$$

$$= C_0 m_{red}^{3/2} \qquad \text{with } m_{red} = \frac{m_A m_B}{m_A + m_B}$$

So finally we have

$$\boxed{\frac{n_A n_B}{n_C} = \frac{(2\pi m_{red} kT)^{3/2}}{h^3} e^{-\beta\Delta}}$$

b)

- We charge neutrality implies

$$\star \quad n_e = n_p$$

- And we must have

$$\star\star \quad n_p + n_H = n \quad \text{constant}$$

- Since the total number of protons (free + bound) is constant, we have from $\star$

$$\frac{n_e n_p}{n_H} = \frac{1}{\lambda_{th}^3} e^{-\beta R} \quad \text{where} \quad \lambda_{th} = \left(\frac{2\pi m_e k_B T}{h^3}\right)^{3/2}$$

$$\frac{n_p^2}{n_H} = \frac{1}{\lambda_{th}^3} e^{-\beta R}$$

- So the ionization fraction $y = n_p/n$ satifies

$$n \frac{y^2}{n_H/n} = \frac{1}{\lambda_{th}^3} e^{-\beta R} \quad \text{note}$$

Now note $n_H/n = 1 - y$ from $\star\star$

So

$$\boxed{\frac{y^2}{1-y} = \frac{1}{n\lambda_{th}^3} e^{-\beta R}}$$

• So Lets substitute #'s

$m_e c^2 = 0.511 \text{ MeV} = 0.5 \times 10^6 \text{ eV}$

$hc = 1240 \text{ eV nm}$

$n = 10^{-7} \text{ nm}^3$

$$\lambda_{th} = \frac{h}{(2\pi m_e k_B T)^{1/2}} = 2.40 \text{ nm}$$

$1/n\lambda_{th}^3 = 7.25 \times 10^5$

$\log(1/n\lambda_{th}^3) = 13.4951$ $\qquad \beta = \frac{1}{kT}$ $\qquad kT = 0.0833 \text{ eV}$

$$\beta R = \frac{13.6 \text{eV}}{\frac{0.025 \text{eV}}{300°\text{K}} \, 1000\text{K}} = 163.2$$

So

$$x \equiv \frac{1}{n\lambda_{th}^3} e^{-\beta R} = e^{13.5 - 163.2} = e^{-150}$$

• This is very small which means, that y will be small.

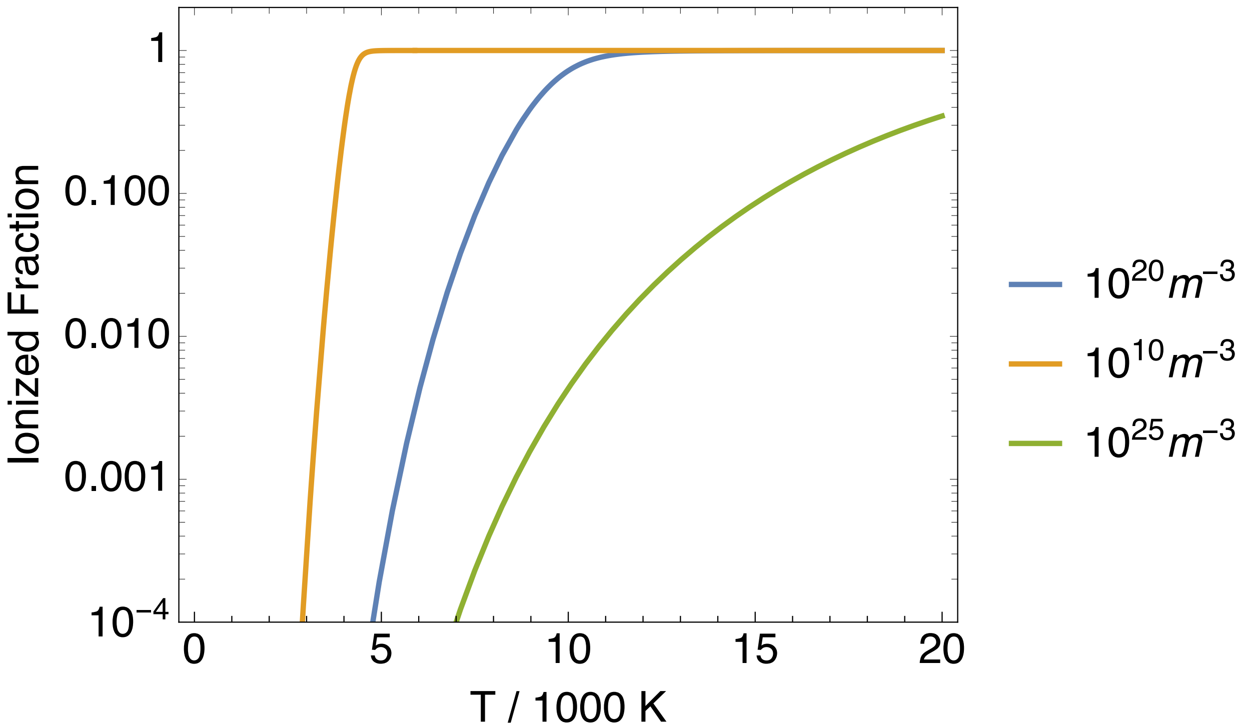
$$\frac{y^2}{1-y} \equiv x$$

$$y \simeq \sqrt{x} \simeq e^{-75} \simeq \boxed{10^{-32.5}}$$

Once can just solve the Saha equation. It is a quadratic equation for y

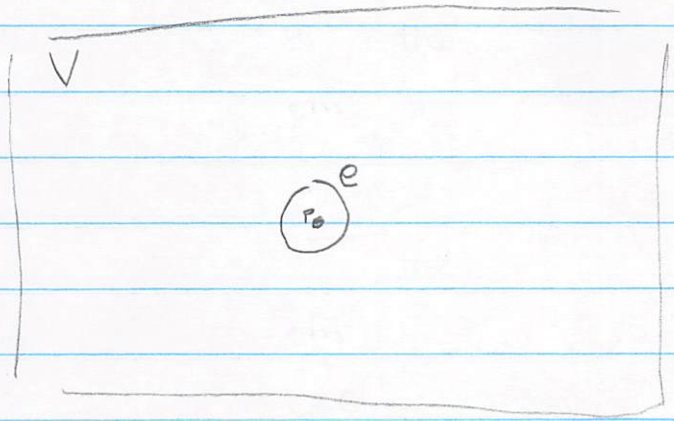
$$y^2 = x(\beta, n)(1 - y)$$

Where $x(\beta, n) = e^{-\ln(n\lambda_{\mathrm{th}}^3) - \beta R}$. I did this and made a graph of the ionization fraction versus temperature. Notice that at low density, the system very rapidly transitions from bound to unbound.



Ionized Fraction
1
0.100
0.010
0.001
10^{-4}
0
5
10
15
20
T / 1000 K
$10^{20} m^{-3}$
$10^{10} m^{-3}$
$10^{25} m^{-3}$

c) To understand the phenomena consider one hydrogen atom in a big box



$$\frac{N}{V} = \frac{1}{V}$$

There is a small amount of phase space of order 1 where the electron is bound, and a large phase-space of order $V p_e^3 / h^3$, where the electron is unbound.

The entropy associated with the unbound states is of order $S/k \sim k \ln \Omega \sim k \ln (V/\lambda_{th}^3)$
So, this grows with the accessible volume when the density is low. Indeed the formula is roughly

$$y^2 \propto e^{(TS_{unbnd} - U)/kT}$$

any y becomes appreciable for $\frac{S}{k_B} \sim \frac{U}{k_B T}$.

So in short the unbound states are penalized energetically, but there are a lot of them, i.e. they are favored entropically.

Neutrality

a) $\mathcal{Z} = \sum_s e^{-\beta(\varepsilon_s - \mu N_s)}$

$$= e^{-\beta(-\Delta/2 - \mu)} + e^{-\beta(\Delta/2 - \mu)}$$

$$+ e^{+\beta\delta/2} + e^{-\beta(\delta/2 - 2\mu)}$$

$$= e^{\beta\mu}\left(e^{\beta\Delta/2} + e^{-\beta\Delta/2}\right) + e^{\beta\delta/2} + e^{2\beta\mu}e^{-\beta\delta/2}$$

$$\boxed{\begin{aligned}\mathcal{Z} &= 2e^{\beta\mu}\cosh(\beta\Delta/2) + e^{\beta\delta/2} + e^{2\beta\mu}e^{-\beta\delta/2} \\ \mathcal{Z} &= 2e^{\beta\mu}\left(\mathrm{ch}(\beta\Delta/2) + \mathrm{ch}(\beta(\delta/2 - \mu))\right)\end{aligned}}$$

b)

$$\bar{N} = \Big[1 \cdot e^{-\beta(-\Delta/2 - \mu)} + 1 \cdot e^{-\beta(\Delta/2 - \mu)}$$

$$+ 2e^{2\beta\mu}e^{-\beta\delta/2}\Big]/\mathcal{Z}$$

So

this can be simplified see last page

$$\boxed{\bar{N} = \frac{2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{2\beta\mu}e^{-\beta\delta/2}}{\mathcal{Z}}}$$

c) Skipped -- included below if really interested.

d) We require $\bar{N} = 1$, or wiriting $\bar{N} = \text{numerator}/\text{den}$

$$2e^{\beta\mu}\cosh(\beta\Delta/2) + 2e^{2\beta\mu}e^{-\beta\delta/2} = 2e^{\beta\mu}\cosh(\beta\Delta/2) + e^{\beta\delta/2}$$

$$+ e^{2\beta\mu}e^{-\beta\delta/2}$$

So we have

$$2e^{2\beta\mu}e^{-\beta\delta/2} = e^{\beta\delta/2} + e^{2\beta\mu}e^{-\beta\delta/2}$$

$$e^{2\beta\mu}e^{-\beta\delta/2} = e^{\beta\delta/2}$$

So $\mu = \delta/2$

e) Lets Find The entropy at the neutrality point

First note that for $\frac{\delta}{2} = \mu$ we have

$$\mathcal{Z} = 2e^{\beta\delta/2}\cosh(\beta\Delta/2) + 2e^{\beta\delta/2}$$

$$= 2e^{\beta\delta/2}(\mathrm{ch}(\beta\Delta/2) + 1) = 4e^{\beta\delta/2}\,\mathrm{ch}^2(\beta\Delta/4)$$

Now

$$\Phi_G = -k_B T \ln \mathcal{Z} \quad \text{and} \quad S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_\mu$$

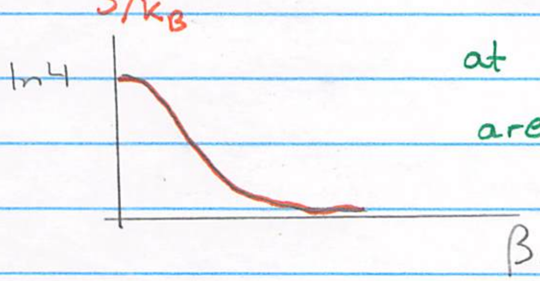
$$\frac{S}{k_B} = \ln \mathcal{Z} + T\frac{\partial}{\partial T}\ln \mathcal{Z}$$

$$= \ln \mathcal{Z} - \beta\frac{\partial}{\partial \beta}\ln \mathcal{Z}$$

$$= \ln(4\,\mathrm{ch}^2(\beta\Delta/4)) + \frac{\beta\delta}{2} - \beta\frac{\partial}{\partial\beta}\left(\frac{\beta\delta}{2} + \ln(4\,\mathrm{ch}^2(\beta\Delta/4))\right)$$

$$\boxed{\frac{S}{k_B} = \ln(4\,\mathrm{ch}^2(\beta\Delta/4)) - \frac{\beta\Delta}{2}\tanh\left(\frac{\beta\Delta}{4}\right)}$$

Sketch



at high T, $\beta\Delta \simeq 0$, and all four states are equally likely and thus the entropy is $\ln 4$. At low T only one state is possible and $\ln(1) = 0 = S$

c) This was a bit more algebra than I intended. You can skip this it won't be graded. A rewrite is given below.

From a) $\mathcal{Z} = 2e^{\beta\mu}\left(\mathrm{ch}\,\beta\Delta/2 + \mathrm{ch}(\beta(\delta/2-\mu))\right)$

Then

$$\Phi_G = -k_B T \ln \mathcal{Z} = U - TS - \mu N$$

So

$$\frac{S}{k_B} = \ln \mathcal{Z} + \beta(U - \mu N)$$

Now

$$\beta(U-\mu N) = -\beta \frac{\partial}{\partial\beta} \ln \mathcal{Z} = -\beta \frac{\partial}{\partial\beta}\left[\beta\mu + \ln\left(\mathrm{ch}(\beta\Delta/2) + \mathrm{ch}\left(\beta\frac{\delta}{2} - \mu\right)\right)\right]$$

$$\beta(U-\mu N) = -\beta\mu - \frac{\beta\Delta/2\,\mathrm{sh}(\beta\Delta/2) - \beta\delta/2\,\mathrm{sh}(\beta(\delta/2-\mu))}{\mathrm{ch}(\beta\Delta/2) + \mathrm{ch}(\beta(\delta/2-\mu))}$$

So

$$\frac{S}{k_B} = \ln\left[2\left(\mathrm{ch}\,\beta\Delta/2 + \mathrm{ch}(\beta(\delta/2-\mu))\right)\right] - \frac{\beta\Delta/2\,\mathrm{sh}(\beta\Delta/2) - \beta\delta/2\,\mathrm{sh}(\beta(\delta/2-\mu))}{\mathrm{ch}(\beta\Delta/2) + \mathrm{ch}(\beta(\delta/2-\mu))}$$

finally from b

$$\boxed{\bar{N} = \frac{ch(\beta\Delta/2) + e^{-\beta(\delta/2-\mu)}}{ch(\beta\Delta/2) + ch(\beta(\delta/2-\mu))}}$$

putting $\mu = \delta/2$ as a sanity check we get

$$\bar{N} = 1$$

and

$$S = \ln[2(ch\beta\Delta/2 + 1)] - \frac{\beta\Delta/2\, sh\,\beta\Delta/2}{ch(\beta\Delta/2) + 1}$$

$$= \ln[4\, ch^2(\beta\Delta/4)] - \frac{\beta\Delta}{2}\, th\,(\beta\Delta/4)$$