CO Poisoning

(1) The quantum concentration is

$$n_Q = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} = 1.65 \times 10^5 \frac{1}{nm^3}$$

Here $m = 32\, m_p$ so using $m_p c^2 = 938\, MeV$ and $k_B = \frac{1/40\, eV}{300\, °K}$ we have with $hc = 1240\, eV\, nm$

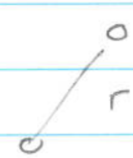
(2) Then we see since $m^{CO} = 28\, m_p$ and $m^{O_2} = 32\, m_p$

$$\frac{n_Q^{CO}}{n_Q^{O_2}} = \left(\frac{m^{CO}}{m^{O_2}}\right)^{3/2} = \left(\frac{28}{32}\right)^{3/2} = 0.82$$

so, n_Q^{CO} is 80% of $n_Q^{O_2}$

(3) So taking a bond length of 1 Å

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$



$r = 1 Å \simeq 2a_0$

$$I = \frac{m^O}{2} r^2 = \mu r^2$$

$$\Delta = \frac{\hbar^2}{2\mu r^2}.$$ Now $\mu = 8\, m_p = 16{,}000\, m_e$

So

This is a $\frac{1}{2}$ Rydberg
$R = +13.6\,eV$

$$\Delta = \frac{\hbar^2}{2\times(16000)\,m_e\,(4a_0^2)} = \frac{1}{4\times 16000}\left(\frac{\hbar^2}{2m_e a_0^2}\right)$$

$$= \frac{13.6\,eV}{4\cdot 16000} \simeq 0.0002\,eV$$ ← this is close

(4) $\left\langle \frac{L^2}{2I} \right\rangle = \left\langle \frac{l(l+1)\,\hbar^2}{2I} \right\rangle = 2\times\frac{1}{2}kT$

← 2 dof in rotation

So neglecting one in $l(l+1)$

$$l^2 = \frac{kT}{\Delta} \qquad \Delta \equiv \frac{\hbar^2}{2I}$$

$$l = \sqrt{\frac{kT}{\Delta}} = \left(\frac{1/40\,eV}{0.0002\,eV}\right)^{1/2} \simeq 12$$

So l is pretty large and a classical approximation is good.

(5.1) $$Z_{rot} = \sum_{l}\sum_{m=-l}^{l} e^{-l(l+1)\Delta\beta}$$

$$= \sum_{l=0}^{\infty}(2l+1)\,e^{-l(l+1)\Delta\beta} \simeq \int_0^{\infty} dl\; 2l\, e^{-l^2\Delta\beta}$$

$$= -\frac{e^{-l^2\Delta\beta}}{\Delta\beta}\Bigg|_0^{\infty} = \frac{1}{\Delta\beta}$$

Now substitute #'s using the #'s in the table and

$$\frac{kT}{\Delta_{O_2}} = 139 \qquad \frac{kT}{\Delta_{CO}} = 104$$

5.3) $\mu_{O_2} = -0.5569\ eV$

5.4) $\mu_{CO} = -0.7173\ eV$ we used $n_{CO} = \frac{n}{1000}$

(6) We have

$$Z_G = 1 + e^{-\beta(\varepsilon_1 - \mu_{O_2})} + e^{-\beta(\varepsilon_2 - \mu_{CO})}$$

$$Z_G = 1 + c_1 + c_2$$

(for example $c_1 \equiv e^{-\beta(\varepsilon_1 - \mu_{O_2})}$)

$c_1 = 41.4$, $\varepsilon_1 = -0.65\ eV$

$c_2 = 201$, $\varepsilon_2 = -0.85\ eV$

$$\boxed{P_1 = c_1/(1 + c_1 + c_2) \qquad P_1 = 0.17}$$

(7) In the limit of low concentration

$$\mu_{CO} \longrightarrow -\infty \quad \text{and} \quad e^{\beta\mu_{CO}} \to 0$$

Then $c_2 \to 0$ and

$$Z_G \simeq 1 + c_1 \quad \text{and} \quad \boxed{P_1 = \frac{c_1}{1 + c_1} \sim 0.975}$$

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

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

Then

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

So

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

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

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

$e^{+(\mu_A + \mu_B - \mu_c)/kT} = 1$ 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 $n_Q = (2\pi m kT)^{3/2}/h^3$

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

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

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

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

$$\text{☆} \quad n_e = n_p$$

- And we must have

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

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

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

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

- 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 ☆☆
So

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

• So Lets substitute #'s

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

$hc = 1240 \text{ eV nm}$

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

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

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

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

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

So

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

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

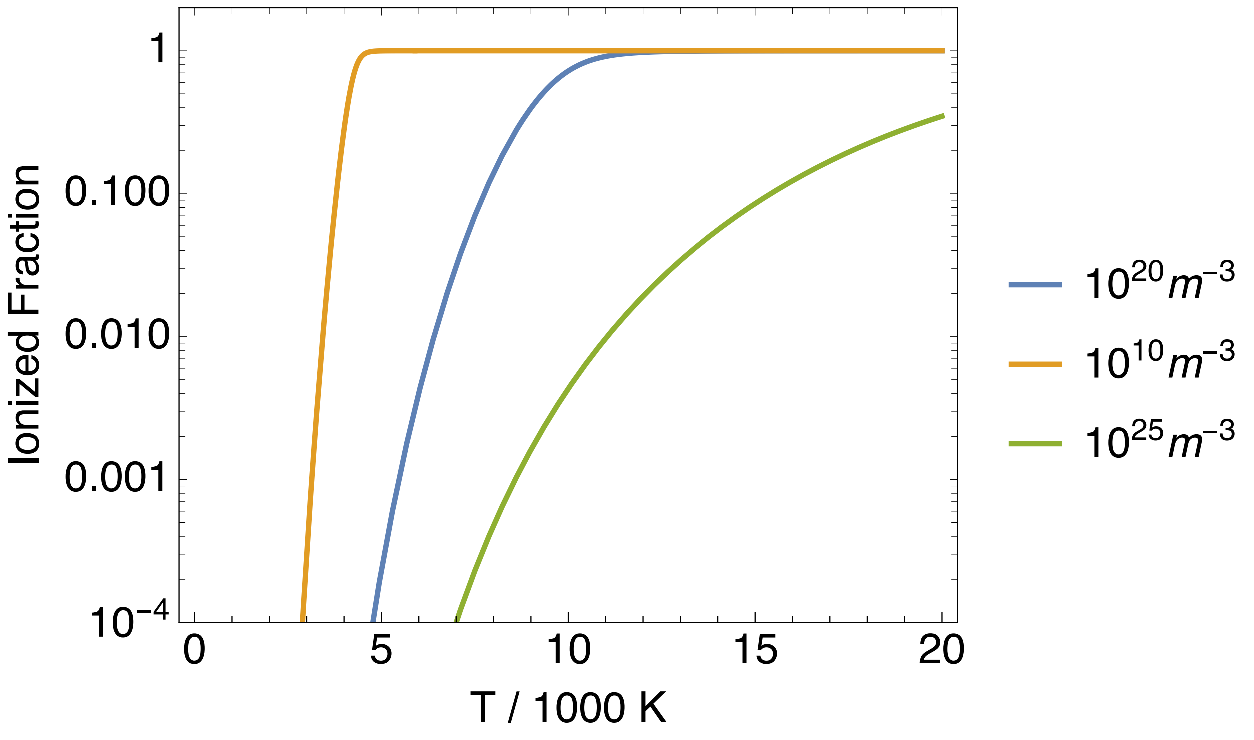
$\dfrac{y^2}{1-y} \equiv x$

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

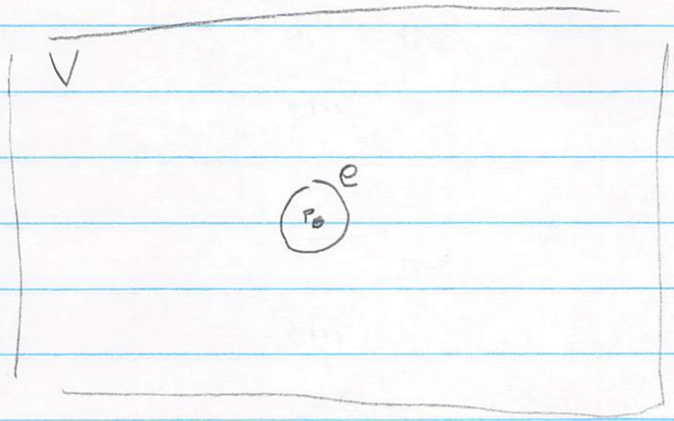
Once can just solve the Saha equation. It is a quadratic equation for y

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

Where $x(\beta, n) = e^{-\ln(n\lambda_{\text{th}}^3) - \beta R}$. 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.