Zhi Chen HW#7

26) A weakly interacting gas:

Consider a weakly interacting gas with partition function:

$$Q = \frac{1}{N!}\left(\frac{V-Nb}{\lambda_{th}^3}\right)^N \exp\left\{\frac{N^2 a}{Vk_BT}\right\}$$

a) Show A is extensive.

$$A = -k_BT \ln Q$$

$$A = -k_BT \ln\left(\frac{1}{N!}\left(\frac{V-Nb}{\lambda_{th}^3}\right)^N \exp\left\{\frac{N^2a}{Vk_BT}\right\}\right)$$

$$\stackrel{!}{=} -k_BT\left[\ln\left(\frac{1}{N!}\right) + N\ln(V-Nb) - 3N\ln\lambda_{th} + \frac{N^2a}{Vk_BT}\right]$$

If we increase N, V by m then A should also changed by m.

$$A_m = -k_BT\left(\ln\frac{1}{(mN)!} + mN\ln(mV-mNb) - 3mN\ln\lambda_{th} + \frac{(mN)^2a}{mVk_BT}\right)$$

$$\stackrel{/}{=} -k_BT\left(-\ln(mN)! + mN(\ln m + \ln(V-Nb)) - 3mN\ln\lambda_{th} + m\frac{N^2a}{Vk_BT}\right)$$

$$\stackrel{!}{=} -k_BT\Big[-mN\ln(\cancel{m}N) + mN + \cancel{mN\ln m} + mN\ln(V-Nb)$$
$$-3mN\ln\lambda_{th} + m\frac{N^2a}{Vk_BT}\Big]$$

$$\stackrel{!}{=} -k_BT\Big[-mN\ln N + mN + mN\ln(V-Nb) - 3mN\ln\lambda_{th}$$
$$+ m\frac{N^2a}{Vk_BT}\Big]$$

$$\stackrel{1}{=} -mk_BT\Big(\underbrace{-N\ln N + N}_{\ln\frac{1}{N!}} + N\ln(V-Nb) - 3N\ln\lambda_{th} + \frac{N^2 a}{Vk_BT}\Big)$$

$$\boxed{A_m \stackrel{1}{=} mA}$$

Change N, V by factor m, leads to changing A by factor m, so A is extensive, as it increases linearly with system.

b) Find EoS: βpV:

$$dA = -SdT - pdV + \mu dN$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$p = \frac{-\partial}{\partial V}\left(-k_BT\left[\cancel{\ln\frac{1}{N!}} + N\ln(V-Nb) - \cancel{3N\ln\lambda_{th}} + \frac{N^2 a}{Vk_BT}\right]\right)_{T,N}$$

$$p = Nk_BT\left(\frac{1}{V-Nb} - \frac{Na}{V^2 k_BT}\right)$$

$$p = \frac{Nk_BT}{V-Nb} - \frac{N^2 a}{V^2}$$

$$\boxed{\beta pV = \frac{NV}{V-Nb} - \frac{N^2 a}{Vk_BT}}$$

Van der Waals EoS:

$$\left(p + \frac{n^2 a}{V^2}\right)\left(V - nb\right) = nRT$$

$$\hookrightarrow \quad p + \frac{n^2 a}{V^2} = \frac{nRT}{V - nb}$$

$$\boxed{\hookrightarrow \quad p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}}$$

it has the same form as

$$p = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}$$

c)

$$\langle (\delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$$

Find $\langle N \rangle$, use grand canonical ensemble.

$$\langle N \rangle = \sum_i P_i N_i$$

$$\overset{!}{=} \sum \frac{e^{-\beta(E_i - \mu N_i)}}{\Xi} N_i$$

$$\overset{!}{=} \frac{1}{\Xi} \frac{1}{\beta} \frac{\partial}{\partial \mu} e^{-\beta(E_i - \mu N_i)}$$

$$\overset{!}{=} \frac{1}{\Xi} \frac{1}{\beta} \left(\frac{\partial}{\partial \mu} \Xi \right)$$

$$\langle N^2 \rangle = \sum P_i N_i^2$$

$$\overset{!}{=} \sum \frac{e^{-\beta(E_i - \mu N_i)}}{\Xi} N_i$$

$$\overset{!}{=} \frac{1}{\beta^2} \frac{1}{\Xi} \frac{\partial^2}{\partial \mu^2} e^{-\beta(E_i - \mu N_i)}$$

$$\overset{!}{=} \frac{1}{\beta^2} \frac{1}{\Xi} \frac{\partial^2}{\partial \mu^2} \Xi$$

Then $\langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \frac{1}{\Xi} \frac{\partial^2}{\partial \mu^2} \Xi - \left(\frac{1}{\beta} \frac{1}{\Xi} \frac{\partial}{\partial \mu} \Xi \right)^2$

$$\overset{!}{=} \frac{1}{\beta^2} \left(\frac{1}{\Xi} \frac{\partial^2}{\partial \mu^2} \Xi - \frac{1}{\Xi^2} \left(\frac{\partial}{\partial \mu} \Xi \right)^2 \right)$$

$$\overset{!}{=} \frac{1}{\beta^2} \frac{\partial}{\partial \mu} \underbrace{\left[\frac{1}{\Xi} \frac{\partial}{\partial \mu} \Xi \right]}_{\beta \langle N \rangle}$$

$$\hookrightarrow \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta^2}\frac{\partial}{\partial\mu}\left(\cancel{\beta}\langle N\rangle\right)$$

$$\overset{!}{=} \frac{1}{\beta}\frac{\partial}{\partial\mu}\left(\langle N\rangle\right)_{T,V}$$

Gibbs-Duhem: $0 = SdT - Vdp + Nd\mu$

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dp$$

$$\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = \frac{V}{N}\left(\frac{\partial p}{\partial N}\right)_{T,V}$$

for $N = \rho V$

$$dN = \rho dV + Vd\rho$$

$$(dN)_V = Vd\rho$$

$$\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = \frac{V}{N}\frac{1}{V}\left(\frac{\partial p}{\partial\rho}\right)_{T,V}$$

$$\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = \frac{1}{N}\left(\frac{\partial p}{\partial\rho}\right)_{T,V}$$

then $\left(\frac{\partial N}{\partial\mu}\right)_{T,V} = N\left(\frac{\partial\rho}{\partial p}\right)_{T,V}$

$$\hookrightarrow \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta}\left(\frac{\partial}{\partial\mu}\langle N\rangle\right)_{T,V}$$

$$\boxed{\langle(\delta N)^2\rangle \overset{!}{=} \langle N\rangle\left(\frac{\partial\beta p}{\partial\rho}\right)^{-1}_{T,V}}$$

use pressure relation from part b:

$$\left(\frac{\partial p}{\partial \rho}\right)_{T,V} = \left(\frac{\partial}{\partial \rho} \frac{Nk_BT}{V-Nb} - \frac{N^2 a}{V^2}\right)_{T,V}$$

$$\stackrel{!}{=} \left(\frac{\partial}{\partial \rho} \left(\frac{\frac{1}{V} Nk_BT}{\frac{1}{V}(V-Nb)} - \rho^2 a\right)\right)_{T,V}$$

$$\stackrel{!}{=} \frac{\partial}{\partial \rho}\left(\frac{\rho k_B T}{1-\rho b} - \rho^2 a\right)_{T,V}$$

$$\stackrel{!}{=} \frac{(k_BT)(1-\rho b) + b\rho k_B T}{(1-\rho b)^2} - 2\rho a$$

$$\stackrel{!}{=} k_BT\left[\frac{(1-\cancel{\rho b}) + \cancel{\rho b}}{(1-\rho b)^2}\right] - 2\rho a$$

$$\langle \delta N^2 \rangle = \langle N \rangle \left(\beta \frac{\partial p}{\partial \rho}\right)^{-1}_{T,V}$$

$$\langle \delta N^2 \rangle \stackrel{!}{=} \langle N \rangle \left[\cancel{\beta k_B T} \frac{1}{(1-\rho b)^2} - 2\rho a\right]^{-1}$$

$$\stackrel{!}{=} \langle N \rangle \left(\frac{1}{(1-\rho b)^2} - \frac{(2\rho a)(1-\rho b)^2}{(1-\rho b)^2}\right)^{-1}$$

$$\boxed{\langle \delta N^2 \rangle = \langle N \rangle \frac{(1-\rho b)^2}{1-2\rho a(1-\rho b)^2}}$$

with ideal gas:

$$pV = Nk_BT$$
$$p = \rho k_BT$$
$$\left(\frac{\partial p}{\partial \rho}\right)_{T,V} = k_BT$$

then
$$\langle \delta N^2 \rangle = \langle N \rangle \left(\beta \frac{\partial p}{\partial \rho}\right)^{-1}_{T,V}$$
$$= \langle N \rangle \left(\underbrace{\cancel{\beta k_BT}}_{=1}\right)^{-1}_{T,V}$$

$$\boxed{\langle \delta N^2 \rangle = \langle N \rangle \quad \leftarrow \text{Poisson. for ideal gas}}$$

We see that compared to ideal gas there is an extra factor depending on parameter, a and b.

27) <u>First Molecule:</u>

Consider a plasma in the classical, low density, high temperature limit. Only consider the ground electronic state. Assume overall # density of protons (H and H^+) $\rho_0 = 10^4\ cm^{-3}$

a) $H^+ + e^- \rightleftharpoons H \quad (\Delta\varepsilon = -13.606\,eV)$

$$K_1 = \frac{\rho_H}{\rho_{H^+}\rho_e}$$

$$= \frac{(q_H)/V}{(q_{H^+})/V\ (q_e)/V}$$

$$= \frac{(q_{trans}\,q_{elec})^H/V}{\frac{(q_{trans}\,q_{elec})^{H^+}}{V}\ \frac{(q_{trans}\,q_{elec})^e}{V}}$$

$$= e^{-\beta\Delta\varepsilon_{elec}} \frac{\cancel{4}\ \frac{\cancel{V}}{\lambda_{th}^3{}_H}\ \frac{1}{\cancel{V}}}{\left(\cancel{2}\ \frac{\cancel{V}}{\lambda_{th}^3{}_{H^+}}\ \frac{1}{\cancel{V}}\right)\left(\cancel{2}\ \frac{\cancel{V}}{\lambda_{th}^3{}_e}\ \frac{1}{\cancel{V}}\right)}$$

$\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$

$$= e^{-\beta\Delta\varepsilon_{el}} \left(\frac{h^2}{2\pi k_B T}\right)^{3/2} \left(\frac{\cancel{m_p + m_e}}{\cancel{m_p}\ m_e}\right)^{3/2}$$

$m_p + m_e \approx m_p$

$$\boxed{K_1 = e^{\beta(13.606eV)}\left(\frac{h^2}{2\pi k_B T\, m_e}\right)^{3/2}}$$

$$He^{2+} + e^- \rightleftharpoons He^+ \qquad \Delta\varepsilon_{elec} = -54.417\,eV$$

$$K_2 = \frac{\rho_{He^+}}{\rho_{He^{2+}}\ \rho_e}$$

$$\overset{!}{=} \frac{(q_{elec})_{He^+}}{(q_{elec})_{He^{2+}}\,(q_{elec})_e} \frac{(\cancel{V}/\lambda_{th}^3)_{He^+}\ \cancel{\frac{1}{V}}}{\cancel{\frac{1}{V}}(\cancel{V}/\lambda_{th}^3)_{He^{2+}}\ (V/\lambda_{th}^3)_e\ \cancel{\frac{1}{V}}}$$

$$\overset{!}{=} e^{-\beta\Delta\varepsilon_{el}}\ \frac{32}{(16)(2)} \left(\frac{h^2}{2\pi k_B T}\right)^{3/2} \left(\frac{\cancel{m_{He^+}}}{\cancel{m_{He^{2+}}}\ m_e}\right)^{3/2}$$

$$\boxed{K_2 \overset{!}{=} e^{-\beta(-54.417eV)} \left(\frac{h^2}{2\pi k_B T m_e}\right)^{3/2}}$$

$$He^{2+} + 2e^- \rightleftharpoons He \qquad \Delta\varepsilon_{elec} = -(24.587+54.417)eV$$

$$K_3 = \frac{\rho_{He}}{\rho_{He^{2+}}\ \rho_e^2}$$

$$\overset{!}{=} \frac{(q_{elec})_{He}}{(q_{elec})_{He^{2+}}\,(q_{elec})_e^2} \frac{\cancel{\frac{1}{V}}\ (\cancel{V}/\lambda_{th}^3)_{He}}{\cancel{\frac{1}{V}}(\cancel{V}/\lambda_{th}^3)_{He^{2+}}\ (V/\lambda_{th}^3)_e^2\ (\cancel{\frac{1}{V}})^2}$$

$$\overset{!}{=} e^{-\beta\Delta\varepsilon_{el}}\ \frac{\cancel{64}}{\cancel{(16)}(2)^2} \left(\frac{h^2}{2\pi k_B T}\right)^{3} \left(\frac{\cancel{m_{He}}}{\cancel{m_{He^{2+}}}\ m_e^2}\right)^{3/2}$$

$$\boxed{\begin{gathered} K_3 \overset{!}{=} e^{-\beta\Delta\varepsilon_{elec}} \left(\frac{h^2}{2\pi k_B T m_e}\right)^{3} \\ \text{where } \Delta\varepsilon_{elec} = -(24.587+54.417)eV \end{gathered}}$$

b) Calculate ρ_H and ρ_{He} from 10,000 K to 3,000 K.

1) approximate $\rho_{H^+} = \rho_e$

2) Assume no He^{2+}, so $\rho_{He} + \rho_{He^+} = \rho_0/16$

$$K_1 = \frac{\rho_H}{\rho_{H^+}\,\rho_e} \qquad K_2 = \frac{\rho_{He^+}}{\rho_{He^{2+}}\,\rho_e} \qquad K_3 = \frac{\rho_{He}}{\rho_{He^{2+}}\,\rho_e^2}$$

with ① $\rho_{H^+} = \rho_e$

$$K_1 = \frac{\rho_H}{\rho_{H^+}^2} \qquad K_2 = \frac{\rho_{He^+}}{\rho_{He^{2+}}\,\rho_{H^+}} \qquad K_3 = \frac{\rho_{He}}{\rho_{He^{2+}}\,\rho_{H^+}^2}$$

with ②: $\rho_{He^+} = \frac{\rho_0}{16} - \rho_{He}$.

$$K_1 = \frac{\rho_H}{(\rho_{H^+})^2} \qquad K_2 = \frac{\rho_0/16 - \rho_{He}}{\rho_{He^{2+}}\,\rho_{H^+}} \qquad K_3 = \frac{\rho_{He}}{\rho_{He^{2+}}\,\rho_{H^+}^2}$$

Also know $\rho_0 = \rho_H + \rho_{H^+}$ or $\rho_{H^+} = \rho_0 - \rho_H$

↳ $$K_1 = \frac{\rho_H}{(\rho_0 - \rho_H)^2} \qquad K_2 = \frac{\rho_0/16 - \rho_{He}}{\rho_{He^{2+}}\,(\rho_0 - \rho_H)} \qquad K_3 = \frac{\rho_{He}}{\rho_{He^{2+}}(\rho_0 - \rho_H)^2}$$

3 eq, with 3 unknowns, now solve for ρ_H, ρ_{He}.

$$\rho_H = k_1 (\rho_0 - \rho_H)^2$$

$$k_1(\rho_0^2 - 2\rho_0\rho_H + \rho_H^2) - \rho_H = 0.$$

$$k_1\rho_0^2 - 2k_1\rho_0\rho_H - \rho_H + \rho_H^2 k_1 = 0$$

$$\rho_H^2 k_1 - (2k_1\rho_0 + 1)\rho_H + k_1\rho_0^2 = 0$$

$$\rho_H = \frac{(2k_1\rho_0+1) \pm \sqrt{(2k_1\rho_0+1)^2 - 4k_1^2\rho_0^2}}{2k_1}$$

$$\overset{!}{=} \frac{(2k_1\rho_0+1) - \sqrt{\cancel{4k_1^2\rho_0^2} + 4k_1\rho_0 + 1 - \cancel{4k_1^2\rho_0^2}}}{2k_1}$$

$$\boxed{\rho_H \overset{!}{=} \rho_0 + \frac{1}{2k_1}\left(1 - \sqrt{4k_1\rho_0 + 1}\right)}$$

take negative since we expect
ρ_0 be all ρ_H when temperature is low

$$\Rightarrow \rho_{He} = k_3 (\rho_0 - \rho_H)^2 \rho_{He^{2+}}$$

$$\overset{!}{=} k_3 (\rho_0 - \rho_H)^{\cancel{2}} \frac{(\rho_0/16 - \rho_{He})}{k_2 \cancel{(\rho_0 - \rho_H)}}$$

$$\rho_{He} \overset{!}{=} \frac{k_3}{k_2}(\rho_0 - \rho_H)\left(\frac{\rho_0}{16} - \rho_{He}\right)$$

$$\hookrightarrow \left(\frac{k_2}{k_3}\frac{1}{(\rho_0 - \rho_H)} + 1\right)\rho_{He} = \frac{\rho_0}{16}$$

$$\rho_{He} = \left[\frac{k_2}{k_3} \frac{1}{\rho_0 - \rho_H} + 1 \right]^{-1} \frac{\rho_0}{16}$$

$$\stackrel{!}{=} \frac{\rho_0}{16} \left[\frac{k_2}{k_3} \frac{1}{\rho_0 - \rho_H} + \frac{\rho_0 - \rho_H}{\rho_0 - \rho_H} \frac{k_3}{k_3} \right]^{-1}$$

$$\stackrel{!}{=} \frac{\rho_0}{16} \left[\frac{k_3 (\rho_0 - \rho_H)}{k_2 + (\rho_0 - \rho_H) k_3} \right]$$

$$\stackrel{!}{=} \frac{\rho_0}{16} \left[\frac{k_3 \left(\frac{-1}{2k_1}\right)\left(1 - \sqrt{4\rho_0 k_1 + 1}\right)}{k_2 - \frac{1}{2k_1}\left(1 - \sqrt{4\rho_0 k_1 + 1}\right) k_3} \right]$$

$$\boxed{\rho_{He} \stackrel{!}{=} \frac{\rho_0}{16} \left[\frac{1 - \sqrt{4\rho_0 k_1 + 1}}{1 - \sqrt{4\rho_0 k_1 + 1} - \frac{2k_1 k_2}{k_3}} \right]}$$

c) $H + H^+ \rightleftharpoons H_2^+$

$$K_4 = \frac{\rho_{H_2^+}}{\rho_{H^+}\,\rho_H}$$

$$\stackrel{!}{=} \frac{(q_{trans}\, q_{elec}\, q_{vib}\, q_{rot-nuc\ spin})_{H_2^+}\left(\frac{1}{V}\right)}{\frac{1}{V}(q_{trans}\, q_{elec})_{H^+}\,(q_{trans}\, q_{elec})_{H}\,\frac{1}{V}}$$

$$\stackrel{!}{=} \underset{g_e}{(2)}\, e^{-\beta\Delta\varepsilon_{el}}\,(8)\,\frac{\left[\frac{\cancel{V}}{\lambda_{H_2}^3}\left(\exp\left\{\frac{\hbar\omega}{2k_BT}\right\}-\exp\left\{\frac{-\hbar\omega}{2k_BT}\right\}\right)^{-1}\frac{(2I_{H^+}+1)(2I_H+1)}{2}\,\frac{T}{\Theta_{rot}}\right]_{H_2^+}\frac{1}{\cancel{V}}}{2\frac{1}{\cancel{V}}\left(\frac{\cancel{V}}{\lambda_{H}^3}\right)_{H^+}\ 4\frac{1}{\cancel{V}}\left(\frac{\cancel{V}}{\lambda_{H}^3}\right)_{H}}$$

$$\stackrel{!}{=} 2e^{-\beta\Delta\varepsilon_{el}}\left(\exp\left\{\frac{\hbar\omega}{2k_BT}\right\}-\exp\left\{\frac{-\hbar\omega}{2k_BT}\right\}\right)^{-1}\left(\frac{h^2}{2\pi k_BT}\right)^{3/2}\left(\frac{m_{H_2^+}}{m_{H^+}\,m_H}\right)^{3/2}$$

$I_H = 1/2$

$$\frac{(2I_{H^+}+1)(2I_H+1)}{2}\,\frac{T}{\Theta_{rot}}\left(\frac{1}{2}\right)\left(\frac{1}{4}\right)(8)$$

$$\stackrel{!}{=} 2e^{-\beta\Delta\varepsilon_{el}}\left(\exp\left\{\frac{\hbar\omega}{2k_BT}\right\}-\exp\left\{\frac{-\hbar\omega}{2k_BT}\right\}\right)^{-1}\left(\frac{h^2}{2\pi k_BT}\right)^{3/2}$$

$$\left(\frac{(2(\frac{1}{2})+1)(2(\frac{1}{2})+1)}{2}\right)\frac{2I_0 k_BT}{\hbar^2}\left(\frac{2m_p+m_e}{(m_p+m_e)(m_p)}\right)^{3/2}$$

use $I_0 = \mu r^2$

$$\stackrel{!}{=} e^{-\beta\Delta\varepsilon_{el}}\left[\exp\left\{\frac{\hbar\omega}{2k_BT}\right\}-\exp\left\{\frac{-\hbar\omega}{2k_BT}\right\}\right]^{-1}\left(\frac{h^2}{2\pi k_BT}\right)^{3/2}$$

$$\frac{8\, r^2 k_BT}{\hbar^2}\left(\frac{2m_p+m_e}{(m_p+m_e)\,m_p}\right)^{3/2}\left(\frac{(m_p+m_e)(m_p)}{2m_p+m_e}\right)$$

$$\overset{!}{=} e^{-\beta\Delta\varepsilon_{el}} \left[\exp\left\{\frac{\hbar w}{2k_BT}\right\} - \exp\left\{\frac{-\hbar w}{2k_BT}\right\}\right]^{-1} \left(\frac{h^2}{2\pi k_BT}\right)^{3/2}$$

$$\frac{8 r^2 k_BT}{\frac{h^2}{4\pi^2}} \left(\frac{\cancel{2m_p + m_e}}{\cancel{(m_p+m_e)}m_p}\right)^{1/2}$$

$$\overset{!}{=} e^{-\beta\Delta\varepsilon_{el}} \left[\exp\left\{\frac{\hbar w}{2k_BT}\right\} - \exp\left\{\frac{-\hbar w}{2k_BT}\right\}\right]^{-1} h r^2 \sqrt{\frac{\pi}{k_BT}} \sqrt{2}\ 8\sqrt{\frac{2}{m_p}}$$

$$e^{-\beta\Delta\varepsilon_{el}} = \frac{e^{-\beta(-D_e)}}{e^{-\beta(-13.606eV)}}$$

$$\boxed{K_4 \overset{!}{=} e^{-\beta(-D_e+13.606eV)} \left[\exp\left\{\frac{\hbar w}{2k_BT}\right\} - \exp\left\{\frac{-\hbar w}{2k_BT}\right\}\right]^{-1} h r^2 \sqrt{\frac{\pi}{m_p k_BT}}\ 16}$$

$$H + H \rightleftharpoons H_2$$

$$K_5 = \frac{q_{H_2}}{q_H^{\,2}}$$

$$= \frac{(q_{trans}\, q_{elec}\, q_{vib}\, q_{rot-nuc\text{-}spin})\frac{1}{V}}{(q_{Htrans})\frac{1}{V}}$$

$$= e^{-\beta\Delta\varepsilon} \frac{\cancel{16}\, q_{vib}\, \frac{(2I_A+1)(2I_B+1)}{2}\, \frac{2\mu r^2 k_B T}{\hbar^2}\, \frac{\cancel{V}}{\cancel{\lambda_{th}^3}}\, \cancel{\frac{1}{V}}}{\left(\cancel{4}\, \frac{\cancel{V}}{\cancel{\lambda_{th}^3}}\, \cancel{\frac{1}{V}}\right)^2}$$

$I_A = I_B = \frac{1}{2}$

$$= e^{-\beta\Delta\varepsilon} q_{vib} \frac{4\mu r^2 k_B T}{h^2}\, 4\pi^2 \left(\frac{h^2}{2\pi k_B T}\right)^{3/2} \left(\frac{2m_p + 2m_e}{(m_p+m_e)^2}\right)^{3/2}$$

$$= e^{-\beta\Delta\varepsilon} q_{vib} \frac{h r^2}{\sqrt{k_B T}} \sqrt{2\pi}\, 4 \left(\frac{2m_p+2m_e}{(m_p+m_e)^2}\right)^{3/2} \left(\frac{(m_p+m_e)^2}{2(m_p+m_e)}\right)$$

$$= e^{-\beta\Delta\varepsilon} q_{vib} \sqrt{\frac{2\pi}{k_B T}}\, 4 h r^2 \sqrt{\frac{(2\cancel{m_p}+2m_e)}{(m_p+m_e)^2}}$$

$$= e^{-\beta(D_e + 2(13.606\,eV))} \left[\exp\left\{\frac{\hbar\omega}{2k_B T}\right\} - \exp\left\{\frac{-\hbar\omega}{2k_B T}\right\}\right]^{-1} \sqrt{\frac{2\pi}{k_B T}}\, 4 h r^2 \sqrt{\frac{2}{m_p}}$$

$$\boxed{K_5 = e^{-\beta(-D_e + 2(13.606\,eV))} \left[\exp\left\{\frac{\hbar\omega}{2k_B T}\right\} - \exp\left\{\frac{-\hbar\omega}{2k_B T}\right\}\right]^{-1} 8h \sqrt{\frac{\pi}{m_p k_B T}}\, r^2}$$

$$He + H^+ \rightleftharpoons HeH^+$$

$$K_b = \frac{\rho_{HeH^+}}{\rho_{He}\,\rho_{H^+}}$$

$$= e^{-\beta\Delta\varepsilon} \frac{\cancel{(128)}\left(\frac{1}{\cancel{\lambda_{th}^3}}\right) q_{vib}\,(2I_{He}+1)(2I_{H^+}+1)\;\frac{2ur^2 k_BT}{\hbar^2}}{\cancel{64}\left(\frac{1}{\cancel{\lambda_{th}^3}}\right)_{He}\;\cancel{2}\left(\frac{1}{\cancel{\lambda_{th}^3}}\right)_{H^+}}$$

$I_{He}=0$

$I_H = 1/2$

$$= e^{-\beta\Delta\varepsilon} q_{vib}\,\frac{4r^2 k_BT}{\left(\frac{h}{2\pi}\right)^2}\left(\frac{h^2}{2\pi k_BT}\right)^{3/2}\left(\frac{5m_p+2m_e}{(4m_p+2m_e)(m_p)}\right)^{3/2}\left(\frac{(4m_p+2m_e)\,m_p}{5m_p+2m_e}\right)$$

$$= e^{-\beta\Delta\varepsilon} q_{vib}\,\frac{4hr^2}{\sqrt{k_BT}}\sqrt{2\pi}\left(\frac{5m_p+\cancel{2m_e}}{(4m_p+\cancel{2m_e})(m_p)}\right)^{1/2}$$

$$\doteq e^{-\beta\Delta\varepsilon} q_{vib}\sqrt{\frac{2\pi}{k_BT}}\;4hr^2\left(\frac{5}{4m_p}\right)^{1/2}$$

$$\boxed{K_b \doteq e^{-\beta(-D_e+(24.587+54.417)eV)}\left[\exp\left(\frac{\hbar w}{2k_BT}\right)-\exp\left\{\frac{-\hbar w}{2k_BT}\right\}\right]^{-1} 4hr^2\sqrt{\frac{5\pi}{2k_BT\,m_p}}}$$

d) Calculate ρ_{HeH^+}, $\rho_{H_2^+}$ and ρ_{H_2}

$$\boxed{\begin{aligned} \rho_{H_2^+} &= k_4 \rho_{H^+} \rho_H \\ &\overset{!}{=} k_4 (\rho_0 - \rho_H) \rho_H \end{aligned}}$$

know $\rho_H = \rho_0 + \frac{1}{2k_1}\left(1 - \sqrt{4k_1\rho_0 + 1}\right)$ from part b

$$\rho_{H_2^+} = -k_4 \frac{1}{2k_1}\left(1 - \sqrt{4k_1\rho_0 + 1}\right)\left(\rho_0 + \frac{1}{2k_1}\left(1 - \sqrt{4k_1\rho_0 + 1}\right)\right)$$

$$\boxed{\begin{aligned} \rho_{H_2} &= k_5 \rho_H^2 \\ &\overset{!}{=} k_5 \left\{\rho_0 + \frac{1}{2k_1}\left(1 - \sqrt{4k_1\rho_0 + 1}\right)\right\}^2 \end{aligned}}$$

$$\boxed{\begin{aligned} \rho_{HeH^+} &= k_6 \rho_{He} \rho_{H^+} \\ &\overset{!}{=} k_6 \rho_{He} (\rho_0 - \rho_H) \\ &\overset{!}{=} -k_6 \frac{1}{2k_1}\left(1 - \sqrt{4k_1\rho_0 + 1}\right) \frac{\rho_0}{\rho_6}\left[\frac{1 - \sqrt{4\rho_0 k_1 + 1}}{1 - \sqrt{4\rho_0 k_1 + 1} - \frac{2k_1k_2}{k_3}}\right] \end{aligned}}$$