Problem 1.

part a. Heat Entropy

part b.

\[ \Delta \sigma = 0 = \left( \frac{Q_{hh}}{\tau_{hh}} - \frac{Q_h}{\tau_h} \right) + \left( \frac{Q_l}{\tau_l} - \frac{Q_l + Q_{hh} - Q_h}{\tau_h} \right) \]

\[ = -Q_{hh} \left( \frac{1}{\tau_h} - \frac{1}{\tau_{hh}} \right) + Q_l \left( \frac{1}{\tau_l} - \frac{1}{\tau_h} \right) \]

\[ \Rightarrow \frac{Q_l}{Q_{hh}} = \frac{\tau_l (\tau_{hh} - \tau_h)}{\tau_h (\tau_h - \tau_l)} \]

Problem 2. Yes, because \( \gamma C = \frac{Q_l}{W} = \frac{T_i}{T_i - T_l} \) can be made arbitrarily large by making the refrigerator temperature \( T_i \) arbitrarily close to the room temperature \( T_h \).

Problem 3. At temperature \( T_i \), the differential amounts of heat removed and work done on the system are related by \( \frac{dQ}{dW} = \frac{T_i}{T_i - T_l} \), where \( T_i \) is the initial temperature, equal to room temperature. Since the sign convention used for \( dQ \) is the opposite of our usual convention, with heat taken out of the system considered positive, we have \( C = -dQ/dT \), or \( dQ = -CdT \). Thus the total work is given by

\[ W = \int_{T_l}^{T_i} \frac{T_i - T}{T} dQ = -\int_{T_l}^{T_i} \frac{T_i - T}{T} CdT = \int_0^{T_i} \frac{T_i - T}{T} CdT \]

\[ = \int_0^{T_i} \frac{T_i - T}{T} aT^3 dT = \int_0^{T_i} (aT_iT^2 - aT^3) dT = \frac{aT_i^4}{12} \]

Problem 4.
part a. Maxwell relations are derived by equating the mixed partial derivatives of a function of many variables. For example, for a function \(f(x,y)\), we have
\[
\left( \frac{\partial^2 f}{\partial x \partial y} \right)_y = \left( \frac{\partial^2 f}{\partial y \partial x} \right)_x.
\]
Given \(dG = -\sigma d\tau + V dp + \mu dN\), the first derivatives of \(G\) are
\[
\left( \frac{\partial G}{\partial \tau} \right)_{p,N} = -\sigma, \quad \left( \frac{\partial G}{\partial p} \right)_{\tau,N} = V, \quad \text{and} \quad \left( \frac{\partial G}{\partial N} \right)_{\tau,p} = \mu.
\]
Taking derivatives with respect to \(\tau\) and \(p\) gives
\[
\frac{\partial^2 G}{\partial \tau \partial p} = \left( \frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial p} \right) \right)_{\tau,N} = \left( \frac{\partial}{\partial \tau} V \right)_{p,N} \quad \text{and} \quad \frac{\partial^2 G}{\partial p \partial \tau} = \left( \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial \tau} \right) \right)_{p,N} = \left( \frac{\partial}{\partial p} (-\sigma) \right)_{\tau,N}
\]
\[
\Rightarrow -\left( \frac{\partial \sigma}{\partial p} \right)_{\tau,N} = \left( \frac{\partial V}{\partial \tau} \right)_{p,N}.
\]
Repeating with \(\tau\) and \(N\) gives
\[
-\left( \frac{\partial \sigma}{\partial N} \right)_{\tau,p} = \left( \frac{\partial \mu}{\partial \tau} \right)_{p,N},
\]
and repeating with \(p\) and \(N\) gives
\[
\left( \frac{\partial V}{\partial N} \right)_{\tau,p} = \left( \frac{\partial \mu}{\partial p} \right)_{\tau,N}.
\]

part b.
\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial \tau} \right)_{p,N} = -\frac{1}{V} \left( \frac{\partial \sigma}{\partial p} \right)_{\tau,N}
\]
In the limit \(\tau \to 0\), the Third Law of Thermodynamics says that \(\sigma\) approaches a constant value, independent of \(p\). Thus, at \(\tau = 0\), the derivative on the right hand side is zero, and \(\alpha = 0\).

**Problem 5.**

**part a.** For all \(N\), we have
\[
\frac{[N][1]}{[N + 1]} = K_N.
\]
For \(N = 1\),
\[
\frac{[1][1]}{[2]} = K_1 \Rightarrow [1 + 1] = \frac{[1]^{1+1}}{K_1}.
\]
For an arbitrary $N$, assume that $[N + 1] = [1]^{N+1}(K_1 \cdots K_N)^{-1}$. Then

$\frac{[N + 1]^{[1]}}{[N + 2]} = K_{N+1}$

$\Rightarrow \frac{[N + 2]}{[N + 1]} = \frac{1}{K_{N+1}}$

$\Rightarrow [N + 2] = \frac{[N + 2][N + 1]}{[N + 1]} = \frac{[1]}{K_{N+1}} K_1 \cdots K_N = \frac{[1]^{N+2}}{K_1 \cdots K_{N+1}}$.  

Thus, by mathematical induction, $[N + 1] = [1]^{N+1}(K_1 \cdots K_N)^{-1}$ must be true for all $N \geq 1$.

**part b.** From the text,

$K(\tau) = \prod_j n_{Q;j}^e \exp(-\nu_j F_j(\text{int})/\tau)$.

For the reaction $(N)\text{mer} + \text{monomer} \rightarrow (N + 1)\text{mer}$, we have $\nu_1 = \nu_N = 1$, and $\nu_{N+1} = -1$. Then

$K = \frac{n_{Q,N} n_{Q,1} e^{-eF_N + F_1}/\tau}}{n_{Q,N+1} e^{-eF_{N+1}/\tau}} = \frac{n_{Q,N} n_{Q,1} e^{e(F_N + F_1 - F_{N+1})/\tau}}{n_{Q,N+1}}$.

**part c.** At large $N$, $n_{Q,N} \approx n_{Q,N+1}$, so $K \approx n_{Q,1} e^{\Delta F/\tau}$, where $\Delta F = F_{N+1} - F_N - F_1$. Assuming $\Delta F = 0$, we can further approximate $K \approx n_{Q,1}$. Then

$\frac{[N + 1]}{[N]} = \frac{[1]}{K n_{Q,1}} = \frac{1}{[1] n_{Q,1}} = 1 \cdot \left(\frac{2\pi \hbar^2}{M_1 \tau}\right)^{3/2} = 3.75 \times 10^{-8}$

**part d.** Since $\Delta F$ can no longer be neglected, $K \approx n_{Q,1} e^{\Delta F/\tau}$. Then

$\frac{[N + 1]}{[N]} = \frac{1}{[1]} \left(\frac{2\pi \hbar^2}{M_1 \tau}\right)^{3/2} e^{-\Delta F/\tau} > 1$

$\Rightarrow e^{\Delta F/\tau} < \left(\frac{2\pi \hbar^2}{M_1 \tau}\right)^{3/2}$

$\Rightarrow \Delta F < \tau \log \left(\frac{2\pi h^2}{M_1 \tau}\right)^{3/2} = -6.9 \times 10^{-20} \text{ J} = -0.43 \text{ eV}$

**Problem 6.** If the temperature $\tau$ were much larger than 655 eV, the ionization energy of Ca XIII, then calcium would exist in higher ionization states than XIII, and Ca lines would not be visible. Therefore, $\tau \lesssim 655$ eV.

In order to find a lower bound on $\tau$, we write down the Saha equation for the reactions $Ca_{\text{III}} \rightarrow Ca_{\text{IV}} + e^-$ and $Ca_{\text{V}} \rightarrow Ca_{\text{VI}} + e^-$,

$\frac{[Ca_{\text{IV}}][e^-]}{[Ca_{\text{III}}]} = \frac{2g_{\text{IV}}}{g_{\text{III}} \left(\frac{m_\tau \tau}{2\pi \hbar^2}\right)^{3/2} e^{-I_{\text{III}}/\tau}}$ and

$\frac{[Ca_{\text{VI}}][e^-]}{[Ca_{\text{V}}]} = \frac{2g_{\text{VI}}}{g_{\text{V}} \left(\frac{m_\tau \tau}{2\pi \hbar^2}\right)^{3/2} e^{-I_{\text{V}}/\tau}}$.

Dividing the first equation by the second gives

$\frac{[Ca_{\text{IV}}]}{[Ca_{\text{III}}]} = \left(\frac{g_{\text{IV}} g_{\text{V}}}{g_{\text{III}} g_{\text{VI}}} \left(\frac{e^{I_{\text{III}} - I_{\text{V}}}}{\tau}\right)\right)$. 

\[ \frac{[Ca_{\text{IV}}]}{[Ca_{\text{III}}]} = \left(\frac{g_{\text{IV}} g_{\text{V}}}{g_{\text{III}} g_{\text{VI}}} \left(\frac{e^{I_{\text{III}} - I_{\text{V}}}}{\tau}\right)\right). \]
The first term in parenthesis on the right hand side is expected to be small; the second term will be of order unity; and the final term is greater than one. Since Ca XIII lines are much stronger than Ca XV lines, the quantity on the left hand side must be small. Therefore, the third term on the right hand side should not be too much larger than unity. That is, $\tau$ shouldn’t be much less than $I_{XV} - I_{XIII}$. $\tau \lesssim 159$ eV. Thus we have $159$ eV $\lesssim \tau \lesssim 655$ eV, or $1.8 \times 10^6$ K $\lesssim T \lesssim 7.6 \times 10^6$ K.

Problem 7.

part a.

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = N \left( \log \left( \frac{n_d(V - Nb)}{N} \right) + 1 \right) + N\tau \cdot \frac{3}{2\tau}$$

= $$N \left( \log \left( \frac{n_d(V - Nb)}{N} \right) + \frac{5}{2} \right)$$

part b.

$$U = F + \tau \sigma$$

= $$-N\tau \left( \log \left( \frac{n_d(V - Nb)}{N} \right) + 1 \right) - \frac{N^2a}{V} + N\tau \left( \log \left( \frac{n_d(V - Nb)}{N} \right) + \frac{5}{2} \right)$$

= $$\frac{3}{2}N\tau - \frac{N^2a}{V}$$

part c.

$$H = U + pV = \frac{3}{2}N\tau - \frac{N^2a}{V} + pV$$

= $$\frac{3}{2}N\tau - \frac{N^2a}{V} + \frac{N\tau V}{V - Nb} - \frac{N^2a}{V}$$

$\approx \frac{3}{2}N\tau - \frac{2N^2a}{V} + N\tau + N\tau \left( \frac{Nb}{V} \right)$$

= $$\frac{5}{2}N\tau - \frac{2N^2a}{V} + \frac{N^2b\tau}{V}$$

Since all terms including $V$ already have factors of $a$ or $b$, and we’re only working to first order, we can use the zero order equation for $V$, $V = N\tau/p$. Thus we have

$$H = \frac{5}{2}N\tau - \frac{2Np\tau}{\tau} + Npb$$