1. (a) We consider a reversible refrigerator operating between the temperatures $\tau_\ell$ and $\tau_h$, where the heat extracted from the low-temperature reservoir is $Q_\ell$ and the heat dumped into the high-temperature reservoir is $Q_h$. The corresponding entropies are $\sigma_\ell = Q_\ell / \tau_\ell$ and $\sigma_h = Q_h / \tau_h$. We imagine that the work needed to run this refrigerator, $W$, is supplied by a reversible heat engine operating between the temperatures $\tau_{hh}$ and $\tau_h$, with the heat input labeled $Q_{hh}$ and the heat output labeled $\tilde{Q}_h$, which is independent from $Q_h$. The corresponding entropies are $\sigma_{hh} = Q_{hh} / \tau_{hh}$ and $\tilde{\sigma}_h = \tilde{Q}_h / \tau_h$. The energy and entropy flows are given in the diagram below.

![Diagram of a reversible refrigerator and heat engine](image)

**FIG. 1.**

(b) By conservation of energy we have $Q_{hh} - \tilde{Q}_h = W = Q_h - Q_\ell$. This can be rearranged to give: $Q_h + \tilde{Q}_h = Q_{hh} + Q_\ell$. Since both the refrigerator and engine are reversible, no entropy is generated and we have $\sigma_{hh} = \tilde{\sigma}_h$ and $\sigma_\ell = \sigma_h$. Adding these two equations and using the definitions of the entropies we find

$$\frac{Q_{hh}}{\tau_{hh}} + \frac{Q_\ell}{\tau_\ell} = \frac{\tilde{Q}_h}{\tau_h} + \frac{Q_h}{\tau_h} = \frac{1}{\tau_h} (Q_{hh} + Q_\ell),$$

where in the last step we used $Q_h + \tilde{Q}_h = Q_{hh} + Q_\ell$. Dividing this equation by $Q_{hh}$ gives a single equation in a single unknown, the ratio $Q_\ell / Q_{hh}$:

$$\frac{1}{\tau_{hh}} + \left( \frac{Q_\ell}{Q_{hh}} \right) \frac{1}{\tau_\ell} = \frac{1}{\tau_h} \left( 1 + \frac{Q_\ell}{Q_{hh}} \right).$$

Solving this equation for $Q_\ell / Q_{hh}$ gives

$$\frac{Q_\ell}{Q_{hh}} = \frac{\tau_\ell}{\tau_{hh}} \left( \frac{\tau_{hh} - \tau_h}{\tau_h - \tau_\ell} \right).$$

2. The short answer is yes, the refrigerator can cool to a temperature $\tau_\ell < \tau_{room} \equiv \tau_h$. The reason is that the coefficient of refrigerator performance for a Carnot refrigerator $\gamma_C = \tau_\ell / (\tau_h - \tau_\ell)$, can be arbitrarily large. Recall $\gamma_C = Q_\ell / W = P_\ell / P_C$, where $P_\ell$ is the rate at which heat is pumped out of the low-temperature reservoir and $P_C$ is the power consumed by the refrigerator. Therefore, for a fixed value of $P_C$, which for this problem is 100 W, the rate at which heat is extracted, $P_\ell = \gamma_C P_C$ can be arbitrarily large, i.e. certainly large enough to remove the heat put out by the 100 W bulb and any heat conducted through the walls of the refrigerator. This may seem counterintuitive at first, but note that for $\gamma_C$ to be very large we need $\tau_\ell$ to be very close (but still less than) $\tau_h$. In other words, you can build a refrigerator that runs on 1 $\mu$W of power, but the temperature inside won’t be much smaller than room temperature.
3. For a reversible refrigerator, the differential amount of work, \( dW \), required to remove an amount of heat, \( dQ \), from the low-temperature reservoir, i.e. the solid we are trying to cool, is given by \( dW = dQ / \gamma_C(T) \). In this expression, \( \gamma_C(T) = T / (T_h - T) \) is the Carnot coefficient of refrigerator performance, where \( T_h \) is the (fixed) temperature of the high-temperature reservoir, and \( T \) is the (variable) temperature of the low-temperature reservoir. The heat capacity relates the amount of heat extracted from the solid, \( dQ \), to its change in temperature \( dQ = C(T)dT \), where for this problem \( C(T) = a T^3 \). Therefore, the total amount of work (i.e. electrical energy) required to cool the solid from \( T = T_i = T_h \) to \( T = 0 \) is

\[
W = \int dW = \int \frac{dQ}{\gamma_C} = -\int_{T_i}^{0} dT \frac{C(T)}{\gamma_C(T)} = \int_{T_i}^{0} dT \frac{a T^3(T_i - T)}{T} = a T_i \left( \frac{T_i^4}{3} - \frac{T_i^4}{4} \right) = \frac{a T_i^4}{12}.
\]

4. (a) In general, Maxwell relations follow from second derivatives of a thermodynamic potential, in this case the Gibbs free energy, \( G \). Consider

\[
\frac{\partial}{\partial \tau} \left( \frac{V}{N_p} \right)_{\tau,p} = \frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial p} \right)_{\tau,N} \frac{\partial}{\partial N} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} + \frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} = -\frac{\partial}{\partial p} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p},
\]

where we have used \( V = \left( \frac{\partial G}{\partial p} \right)_{N,\tau} \) and \( \left( \frac{\partial G}{\partial \tau} \right)_{N,p} = -\sigma \), and the fact that the partial derivative operators commute (since the derivatives of \( G \) exist and are continuous). Similarly

\[
\frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial N} \right)_{\tau,p} = \frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,N} \frac{\partial}{\partial N} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} + \frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} = \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} \mu,
\]

where we have used \( V = \left( \frac{\partial G}{\partial \tau} \right)_{\tau,N} \) and \( \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} = -\sigma \). Finally we have,

\[
\frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} = \frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,N} \frac{\partial}{\partial N} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} + \frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} = -\frac{\partial}{\partial \tau} \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} \sigma,
\]

where we have used \( \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} = \mu \) and \( \left( \frac{\partial G}{\partial \tau} \right)_{\tau,p} = -\sigma \).

(b) Given \( \alpha = (1/V)(\partial V/\partial \tau)_p \) and the Maxwell relation \( (\partial V/\partial \tau)_p = -(\partial \sigma/\partial p)_\tau \) we immediately find \( \alpha = (-1/V)(\partial \sigma/\partial p)_\tau \). The third law of thermodynamics states that as \( \tau \to 0 \), \( \sigma \) goes to a constant, and hence \( (\partial \sigma/\partial p)_\tau \to 0 \), and therefore \( \alpha \to 0 \) as \( \tau \to 0 \).

5. (a) From the law of mass action for the basic reaction step we have \( [1]/[N]/[N+1] = K_N \), or rearranging, \( [N+1] = [1]/K_N \). Iterating this expression, i.e. replacing \( N \) with \( N - 1 \) to find \( [N] = [1]/[N - 1]/K_{N - 1} \) and using this to eliminate \( [N] \) in the expression for \( [N+1] \) gives \( [N+1] = [1][N - 1]/K_N K_{N - 1} \). If we iterate a total of \( N \) times we arrive at \( [N+1] = [1]^{N+1}/K_N K_{N - 1} \cdots K_1 \).

(b) Using Eq. (34) from Chap. 9 of K&K we immediately find

\[
K_N = \frac{n_Q(N)n_Q(N+1)}{n_Q(N+1)} \exp\left(\left(F_{N+1} - F_N - F_1\right)/\tau\right),
\]

where \( n_Q(N) = (M_N \tau/2\pi h^2)^{3/2} \) is the quantum concentration of the \( N \)mer.

(c) Given \( N \gg 1 \) so that \( n_Q(N) \approx n_Q(N+1) \), and \( \Delta F = F_{N+1} - F_N - F_1 = 0 \), we have from the results of (a) and (b),

\[
\frac{[N+1]}{[N]} = K_N = \frac{[1]n_Q(N+1)}{n_Q(N)n_Q(N+1)} = \exp(-\Delta F/\tau)
\]

\[
\approx \left[ 1 \right] \left( 2\pi h^2 / M_1 \tau \right)^{3/2} \approx \left[ 1 \right] \left( 2\pi (1.05 \cdot 10^{-27} \text{erg})^2 / (200)(1.67 \cdot 10^{-24} \text{g})(1.38 \cdot 10^{-16} \text{erg K}^{-1})(300 \text{K}) \right)^{3/2} = 3.5 \cdot 10^{-8}.
\]
Using this result to eliminate \( p \) we find \( [N+1]/[N] > 1 \). Thus, \([N+1]/[N] = ([1]/n_Q(1))e^{-\Delta F/\tau} > 1\), which implies

\[
\Delta F < -\tau \log \left[ \frac{1}{[1]} \left( \frac{M_1}{2\pi h^2} \right)^{3/2} \right] \\
= -(1.38 \times 10^{-16} \text{ erg K}^{-1})(300 \text{ K}) \log \left[ \frac{1}{10^{20} \text{ cm}^{-3}} \left( \frac{200)(1.67 \times 10^{-24} \text{ g})(1.38 \times 10^{-16} \text{ erg K}^{-1})(300 \text{ K})}{2\pi(1.05 \times 10^{-24} \text{ erg s}^2)} \right)^{3/2} \right] \\
= -7.1 \times 10^{-13} \text{ erg} = -0.4 \text{ eV}
\]

6. We are asked for an order of magnitude estimate for the temperature of the Sun’s corona. Note we are not given any quantitative information about the relative concentrations of Ca XIII and Ca XV, only that the lines of Ca XIII and much stronger than the lines of Ca XV, which suggests \([\text{Ca XIII}] \gg [\text{Ca XV}]\). From the Saha equation we know that the ratio of the concentration of \((n+1)\)-times ionized Ca to the concentration of \(n\)-times ionized Ca is proportional to the Boltzmann factor \( e^{-\Delta n_{+1,n}/\tau} \), where \( I_{n+1,n} \) is the ionization potential of \(n\)-times ionized Ca. From the information given in the problem we know \( I_{13,12} = 655 \text{ eV}, \) and \( I_{15,14} = 814 \text{ eV}. \) Since we know there is much more Ca XIII in the corona than Ca XV, we can argue that \( \tau \) is somewhere in the neighborhood of \( I_{13,12} \), since if it were much less than this value it would also be much smaller than \( I_{12,11} \) and thus we would not have much Ca XIII, while if it were much greater than this value we would expect to see more Ca XV. Thus \( T_{\text{corona}} \approx I_{13,12}/k_B = (655 \text{ eV})/[(1.38 \times 10^{-16} \text{ erg K}^{-1})(1 \text{ eV}/1.602 \times 10^{-12} \text{ erg})] \approx 8 \times 10^6 \text{ K}. \)

7. (a) From Eq. (38) in Chap. 10 of K&K, the free energy of a van der Waals gas is

\[
F = -N \tau \{ \log[n_Q(V - Nb)/N] + 1 \} - N^2 a/V.
\]

Using \( \sigma = -(\partial F/\partial \tau)_V \) and \( n_Q \propto \tau^{3/2} \), we find the entropy of a van der Waals gas is

\[
\sigma = N \{ \log[n_Q(V - Nb)/N] + 1 \} + N \tau \frac{\partial}{\partial \tau} \log(\tau^{3/2}) = N \{ \log[n_Q(V - Nb)/N] + 5/2 \}.
\]

(b) Since we know \( F \) and \( \sigma \) we can readily find the energy:

\[
U = F + \tau \sigma = -N \tau \{ \log[n_Q(V - Nb)/N] + 1 \} - N^2 a/V + \tau N \{ \log[n_Q(V - Nb)/N] + 5/2 \} = \frac{3}{2}N \tau - \frac{N^2 a}{V}.
\]

(c) The enthalpy is \( H = U + pV = 3N \tau/2 - N^2 a/V + pV \), where we have used the result of (b). To obtain \( H(\tau, V) \) we need to eliminate \( p \) from this expression using the van der Waals equation of state: \( (p + N^2 a/V^2)(V - Nb) = N \tau \).

Solving this equation for \( p \) and working only to first order in \( a, b \) we find

\[
p = \frac{N \tau}{(V - Nb)} - \frac{N^2 a}{V^2} = \frac{N \tau}{V} \left( 1 + \frac{Nb}{V} + O(b^2) \right) - \frac{N^2 a}{V^2} = \frac{N \tau}{V} + \frac{N^2 b}{V^2} - \frac{N^2 a}{V^2} + O(b^2).
\]

Using this result to eliminate \( p \) in our above expression for \( H \) we find

\[
H(\tau, V) = \frac{3N \tau}{2} - \frac{N^2 a}{V} + V \left( \frac{N \tau}{V} + \frac{N^2 b}{V^2} - \frac{N^2 a}{V^2} \right) = \frac{5N \tau}{2} + \frac{N^2 b}{V} - \frac{2N^2 a}{V}.
\]
To obtain $H(\tau,p)$, we note that the corrections to the ideal gas expression for $H(\tau,V)$ given above are first order in $a,b$. Therefore we can use the ideal gas law to eliminate $V$ in favor of $p$ in these terms (i.e. $V = N\tau/p$), since the corrections to the ideal gas law in the van der Waals equation of state are of order $a,b$, and therefore will only produce second-order corrections if we had kept them. Thus, using $V = N\tau/p$ in $H(\tau,V)$ we find

$$H(\tau,p) = \frac{5N\tau}{2} + Nbp - \frac{2N\tau p}{\tau}.$$