From chapter 6 we have the following results for the photon gas:

\[ \langle E \rangle = \left( \frac{8\pi^5 \hbar^4}{15c^3h^3} \right) V T^4 \quad (6.15) \]
\[ P = \frac{1}{3} \langle E \rangle V \quad (6.18) \]
\[ S = \frac{1}{3} \left( \frac{32\pi^5 \hbar^4}{15c^3h^3} \right) T^3 V \quad (6.26) \]

If we let \( \tau = \left( \frac{8\pi^5 \hbar^4}{15c^3h^3} \right) \), then the following result holds to make the following prediction for the Gibbs free energy

\[ G = \langle E \rangle - TS + PV \]
\[ = 2VT^4 - \tau \left( \frac{1}{3} \right) \tau T^3V + \left( \frac{1}{3} \right) \tau T^4 \cdot V \]
\[ = 2VT^4 \left( 1 - \frac{1}{3} + \frac{1}{3} \right) \]
\[ = 0 \]

So yes, the results of chapter 6 are consistent with the chemical potential (and Gibbs free energy) being zero for the photon gas.
2) 
\[ G = -k T N \ln \left( \frac{\alpha T^{5/2}}{P} \right) \]

a) 
\[ S = \left( \frac{\partial G}{\partial T} \right)_{P,N} \quad \text{since} \quad \Delta G = -SDT + Vdp + udn \]
\[ = - \left[ -k_B N \ln \left( \frac{\alpha T^{5/2}}{P} \right) - N k_B T \cdot \frac{5/2}{T} \right] \]
\[ = \frac{5}{2} N k_B \left[ \frac{5}{2} + \ln \left( \frac{\alpha T^{5/2}}{P} \right) \right] \]

b) 
\[ C_p = T \left( \frac{\partial S}{\partial T} \right) \]
\[ = T \frac{\partial^2}{\partial T^2} \left[ \frac{5}{2} N k_B + \frac{5}{2} N k_B \ln \left( \frac{\alpha T^{5/2}}{P} \right) + N k_B \ln \left( \frac{\alpha T^{5/2}}{P} \right) \right] \]
\[ = T \left[ 0 + \frac{5}{2} \frac{N k_B}{T} + 0 \right] \]
\[ C_p = \frac{5}{2} N k_B \]

c) 
\[ V = \left( \frac{\partial G}{\partial P} \right)_{T,N} \]
\[ = \frac{\partial}{\partial P} \left[ N k_B T \ln (P) - N k_B T \ln \left( \frac{\alpha T^{5/2}}{P} \right) \right] \]
\[ = \frac{N k_B T}{P} \]
\[ \Rightarrow \quad PV = N k_B T \]

d) 
\[ E = G - PV + TS \quad \text{(since} \quad G = E + PV - TS) \]
\[ = -N k_B T \ln \left( \frac{\alpha T^{5/2}}{P} \right) + N k_B T \left[ \frac{5}{2} + \ln \left( \frac{\alpha T^{5/2}}{P} \right) \right] - PV \]
\[ = \frac{5}{2} N k_B T - PV = \frac{5}{2} N k_B T - N k_B T \quad \text{(using Eqn. of State from C)} \]
\[ E = \frac{3}{2} N k_B T \]
3) 5.12 Reif

quasi-state = thermally insulated \( \Rightarrow \delta S = 0 \) or
\( S = \text{const} \) and we are after the change in \( T \) associated with a change in pressure.
The question suggests the answer can be

\[
\Delta T = \left( \frac{2T}{2P} \right) \Delta P \quad \text{if } \Delta P \text{ is not too large.}
\]

\( \Rightarrow \) we need to re-express the derivative

\[
\left( \frac{\partial T}{\partial P} \right)_S \text{ maxwell? } \quad T dS + V dP = \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial P} \right)_T
\]

doesn't look too helpful

\[
\Rightarrow \quad \frac{\partial (T, S)}{\partial (P, S)} = \frac{\partial (T, S)}{\partial (P, T)} \frac{\partial (P, T)}{\partial (P, S)} \quad \text{(to get } C_P \text{ in)}
\]

\[
= -\left( \frac{\partial S}{\partial P} \right)_T \frac{T}{C_P} \quad C_P \text{ : heat capacity}
\]

Now try a Maxwell's \( -SdT + VdP \)

\[
\Rightarrow \left( \frac{\partial T}{\partial P} \right)_S = \frac{V}{V} \left( \frac{\partial V}{\partial P} \right) \frac{T}{C_P} = \frac{V dT}{C_P} = \frac{V dT}{m(C_P / m)}
\]

\( m \) : mass of the piece or solid \( (p = \frac{m}{V}) \)

\[
\Rightarrow \left( \frac{\partial T}{\partial P} \right)_S = \frac{\Delta T}{P \cdot C_P} \quad C_P \text{ : specific heat/gm}
\]

\( \rho \) : mass density \( m/V \)

\[
\Rightarrow \Delta T = \frac{\Delta T}{P \cdot C_P} \Delta P
\]
4) Refer (5.14)

First think about what is happening.

\[ \Rightarrow \mathbf{F} \rightarrow \mathbf{E} \uparrow \]

Tensile force

ie if \( L \) is increased (say by stretching it) with an external force \( F \) does negative work
(The force and the displacement are in opposite directions)

\[ \Rightarrow dW = -FdL \]

a) Hence, from the first law we have:

\[ dE = TdS - dW \]

\[ \Rightarrow dS = \frac{dE}{T} + \frac{dW}{T} \]

\[ dS = \frac{1}{T}dE - aT(L-L_0) \]

b) We want a derivative of \( S \) wrt. an external parameter \( \ell \).

This looks like a job for a "Maxwell relation".

But one of these "real" 4 don't do, so make your own (I told you that remembering how to derive them would be more useful than simply memorising the relations themselves)

\[ dE = TdS + FdL \quad \text{(see a)} \]

Consider

\[ \bar{F} = E - ST \]

\[ d\bar{F} = TdS + FdL - SdT - TdS \]

\[ = -SdT + FdL \quad \text{(Helmholtz function for this problem)} \]

\[ \Rightarrow -\left( \frac{\partial \bar{F}}{\partial T} \right)_T = \left( \frac{\partial \bar{E}}{\partial T} \right)_T \]

ie we can get the result
directly from the equation of state:

\[
\left(\frac{\partial S}{\partial T}\right)_L = -\frac{2}{\beta_T} \left[ aT^2 (L-L_0) \right]_L
\]

\[
\Rightarrow \left(\frac{\partial S}{\partial T}\right)_T = -2aT(L-L_0)
\]

c) i.e. we must integrate a TdS relation:

\[
S = S(T,H) \Rightarrow \quad dS = \left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial S}{\partial L}\right)_T dL
\]

\[
= \frac{c_v}{T} dT - \left(\frac{\partial F}{\partial T}\right)_L dL
\]

\[
\Rightarrow dS = b dT - 2aT(L-L_0) dL
\]

\[
\int_{AOC} dS = \int_1^T b dT = b(T-T_0)
\]

\[
\int_{COB} dS = -\int_0^{L_0} 2aT(L-L_0) dL = -2aT \int_0^{L_0} u du = -aT(L-L_0)^2
\]

\[
\Delta S = S(L,T) - S(L_0,H) = \int_{AOC} dS + \int_{COB} dS
\]

\[
S(L,T) - S(L_0,H) = b(T-T_0) - aT(L-L_0)^2
\]

(The book's answer cannot be correct, as it is not correct dimensionally.)
d) **Quasi static & adiabatic (thermally isolated)**

\[ S(T_f, L_f) = S(T_i, L_i) \]

or making use of the result in c)

\[ b(T_f - T_0) - a T_f (L_f - L_0)^2 = b(T_i - T_0) - a T_i (L_i - L_0) \]

\[ T_f \left[ b - a(L_f - L_0)^2 \right] = T_i \left[ b - a(L_i - L_0)^2 \right] \]

\[ T_f = T_i \left( \frac{b - a(L_i - L_0)^2}{b - a(L_f - L_0)^2} \right) \]

Note that what enters here is the magnitude of the deviation from the equilibrium position: 

\[ S = L - L_0 \]

and whether \( T_f \) is bigger or less than \( T_i \) will depend on the relative size of \( |t_i| + |t_f| \) (stretched from length \( L_i \) \( \Rightarrow |t_i| > |t_f| \)) and on the relative size of \( a + b \). But, since entropy must be an increasing function of \( T \), we must have \( (L - L_0) \) as \( b \) for all \( L \). Hence

\[ T_f > T_i \]

\[ \left( \frac{b - a \xi_i^2}{b - a \xi_f^2} \right) \xi_i^2 < \xi_f^2 \]

\[ \Rightarrow b - a \xi_i^2 > b - a \xi_f^2 \]

e) To answer this we need to know how \( C_i \) varies with \( L \), so

\[ \frac{\partial (C_i)}{\partial L} = T \left( \frac{\partial S}{\partial T} \right) = T \left( \frac{\partial S}{\partial L} \right) = T \frac{\partial}{\partial L} \left( \frac{\partial S}{\partial T} \right) \]

Using the result from part b) we then obtain:
\[
\frac{\partial c_L}{\partial t} f = r \frac{\partial}{\partial T} \left[ -2aT(L-L_0) \right]
\]

\[
= -2aT(L-L_0)
\]

\[
\Rightarrow C_L = \int_{L_0}^{L} \left( \frac{\partial c_L}{\partial T} \right)_f dL = -aT(L-L_0)^2 + C_L_0
\]

but we were told that \( C_L_0 = bT \) \( \Rightarrow \)

\[
\left[ \frac{\partial S}{\partial T} \right]_{L=L_0} = \frac{1}{T} \frac{\partial S}{\partial T}
\]

\[
S(T,L) - S(T,L_0) = \int_{T_0}^{T} \frac{C_L(L,T)}{T} \, dT = \int_{L_0}^{L} \left[ b - a(L-L_0)^2 \right] dL
\]

\[
= b(T-T_0) - a(T-T_0)(L-L_0)
\]

\[
S(T_0,L) - S(T_0,L_0) = \int_{L_0}^{L} \left( \frac{\partial S}{\partial L} \right)_0 dL
\]

\[
= \int_{L_0}^{L} -2aT_0(L-L_0) \, dL
\]

\[
= -aT_0(L-L_0)^2
\]

\[
\Rightarrow S(T,L) - S(T,L_0) = b(T-T_0) + a(T_0-T)(L-L_0)^2 - aT_0(L-L_0)^2
\]

\[
S(T,L) - S(T_0,L_0) = b(T-T_0) - a(T-L_0)^2
\]

which does agree with part c).
all apologize, what I really meant to ask
for will be a single expression for the
rate of change of entropy decreases
process; 

\[
\left( \frac{\partial S}{\partial V} \right)_E
\]

To find this we note that:

\[dE = TdS - PdV \quad \Rightarrow \quad dS = \frac{1}{T} dE + \frac{P}{T} dV\]

\[\Rightarrow \left( \frac{\partial S}{\partial V} \right)_E = \frac{P}{T}\]

b) For this path we want:

\[
\left( \frac{\partial T}{\partial V} \right)_E = \frac{\partial (T, E)}{\partial (V, E)} \frac{\partial (V, E)}{\partial (V, S)}
\]

\[= \left[ \left( \frac{\partial S}{\partial V} \right)_S \left( \frac{\partial E}{\partial S} \right)_V - \left( \frac{\partial S}{\partial V} \right)_V \left( \frac{\partial E}{\partial V} \right)_S \right] \left( \frac{\partial S}{\partial E} \right)_V
\]

\[= \left[ \left( \frac{\partial S}{\partial V} \right)_S T + \frac{T}{C_V} P \right] \frac{1}{T}
\]

\[= \left[ \left( \frac{\partial S}{\partial V} \right)_S + \frac{P}{C_V} \right]
\]

\[\left( \frac{\partial T}{\partial V} \right)_S \text{ using Maxwell we get you another expression}
\]

\[\left( \frac{\partial T}{\partial V} \right)_S = -\frac{T}{C_V} \left( \frac{\partial S}{\partial P} \right)_T \cdot \frac{T}{C_V}
\]

\[\Rightarrow \left( \frac{\partial T}{\partial V} \right)_S = \frac{T}{C_V} \left( \frac{\partial S}{\partial P} \right)_T
\]

\[\Rightarrow \left( \frac{\partial S}{\partial V} \right)_E = \frac{1}{C_V} \left[ P - T \left( \frac{\partial P}{\partial T} \right)_V \right]\]
For an ideal gas we have:

\[
\frac{dP}{dT} \bigg|_V = \frac{\partial}{\partial T} \left[ \frac{Nk_B T}{V} \right]_V = \frac{Nk_B}{V} = \frac{P}{T}
\]

Hence for this equation of state we find

\[
\left( \frac{dT}{dV} \right)_T = \left( \frac{1}{c_v} \right) \left[ P - T \frac{\partial P}{\partial T} \right] = 0
\]

**d)**

\[
\Delta T \text{ for a free expansion would then be:}
\]

\[
\Delta T = \int_{V_i}^{V_f} \left( \frac{dT}{dV} \right) dV = \int_{V_i}^{V_f} \frac{1}{c_v} \left[ P - T \left( \frac{\partial P}{\partial T} \right)_V \right] dV
\]

For the Van der Waals gas we have (e.g. "Bocciolone 12.49"): 

\[
\rho = \frac{Nk_B}{(V-Nb)} - a \left( \frac{N}{V} \right)^2
\]

\[
\left( \frac{\partial P}{\partial T} \right)_{V,N} = \frac{Nk_B}{(V-Nb)} \Rightarrow
\]

\[
\rho - T \left( \frac{\partial P}{\partial T} \right)_V = \frac{Nk_B T}{(V-Nb)} - a \left( \frac{N}{V} \right)^2 - \frac{Nk_B T}{(V-Nb)} = -a \frac{N^2}{V^2}
\]

\[
\Rightarrow \Delta T = \frac{aN^2}{c_v} \int_{V_i}^{V_f} \frac{1}{V^2} dV = \frac{aN^2}{c_v} \left[ \frac{1}{V} \right]_{V_i}^{V_f}
\]

\[
\Delta T = \frac{aN^2}{c_v} \left[ \frac{1}{V_f^2} - \frac{1}{V_i^2} \right]
\]

where \( V = V/N \) is the volume per particle. If \( \Delta T \) increases the temperature goes down.

(assuming \( a \) and \( c_v \) are > 0) \( a = 0 \Rightarrow \Delta T = 0 \)