9.1

a) We are given $\gamma(T) = b - cT$, and the values of the constants b and c. We also know that $dU = TdS - pdV + \gamma da$. We want to get an expression for γ in terms of a derivative of the Gibbs free energy, so we must first get an expression for the Gibbs free energy.

$$G = H - TS = U + pV - TS$$
$$dG = dU + pdV + Vdp - TdS - SdT$$
$$= -SdT + Vdp + \gamma da$$

To get an expression for γ in terms of a derivative of the Gibbs free energy, we merely have to take the derivative of G with respect to a at constant T and p.

$$\left(\frac{\partial G}{\partial a}\right)_{p,T} = \gamma$$

b) We know that

$$\left(\frac{\partial S}{\partial a}\right)_{p,T} = \frac{\partial}{\partial a}\left(-\frac{\partial G}{\partial T}\right)$$

Switching the order of the derivatives we get that

$$\left(\frac{\partial S}{\partial a}\right)_{p,T} = -\left(\frac{\partial^2 G}{\partial T \partial a}\right) = -\frac{\partial}{\partial T}\left(-\frac{\partial G}{\partial a}\right) = -\left(\frac{\partial \gamma}{\partial T}\right)_{p,a}$$

But we know that $-\left(\dfrac{\partial \gamma}{\partial T}\right)_{p,a}$ is non-other than c. So $\left(\dfrac{\partial S}{\partial a}\right)_{p,T} = c = 0.167 \ ^{erg}\!/_{cm^2 \ deg}$.

c)

$$\Delta S \approx \left(\frac{\partial S}{\partial a}\right)\Delta a = c\Delta a$$

$$\approx \left(0.167 \ ^{erg}\!/_{cm^2 \ deg}\right)\left(4\overset{o}{A}\right)\left(\frac{1cm}{10^8 \ \overset{o}{A}}\right)^2$$

$$\approx 6.68 \times 10^{-17} \ ^{erg}\!/_{deg}$$

9.3   We are given that $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$, and we are asked to show that this implies that $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$ is

not a function of V. For this, we need only prove that $\dfrac{\partial C_V}{\partial V} = \dfrac{\partial}{\partial V}\left(\dfrac{\partial U}{\partial T}\right)_V = 0$. But we know that we can

permute the order of the derivatives, so we get that $\dfrac{\partial C_V}{\partial V} = \dfrac{\partial}{\partial V}\left(\dfrac{\partial U}{\partial T}\right)_V = \dfrac{\partial}{\partial T}\left(\dfrac{\partial U}{\partial V}\right)_T = \dfrac{\partial}{\partial T}(0) = 0$. Thus,

the constant volume heat capacity of an ideal gas is independent of volume.

9.8 The first thing to note is that if we take the cross derivatives of dU, we end up getting $\left(\dfrac{\partial f}{\partial p_0}\right)_{E,S}$

rather than $\left(\dfrac{\partial p_0}{\partial f}\right)_{E,T}$ which we want. We need to first transform our equation to a new energy variable

$X(T,f,E)$.

$$dU = TdS + fdl + Edp_0$$
$$X = U - TS - fl - Ep_0$$
$$dX = SdT - ldf - p_0 dE$$

Now if we take the cross derivatives we can get an expression for $\left(\dfrac{\partial p_0}{\partial f}\right)_{E,T}$.

$$\left(\dfrac{\partial p_0}{\partial f}\right)_{E,T} = \left(\dfrac{\partial l}{\partial E}\right)_{f,T}$$

This is useful, because we are likely able measure how the length of the crystal changes with the field $\left(\dfrac{\partial l}{\partial E}\right)_{f,T}$.

9.10
a) The first thing to note in this question is that we are considering T and p as variables (which we end up holding constant). That means that we need to use the Gibbs free energy.

$$G = H - TS = U + pV - TS$$
$$dG = dU + pdV + Vdp - TdS - SdT$$
$$= -SdT + Vdp + fdl$$

Now we want to create a Maxwell relation between S and f in order to get a function for S.

$$\left(\frac{\partial^2 G}{\partial l \partial T}\right) = \left(\frac{\partial^2 G}{\partial T \partial l}\right)$$

$$\frac{\partial}{\partial l}\left(\frac{\partial G}{\partial T}\right)_{l,p} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial l}\right)_{T,p}$$

$$-\left(\frac{\partial S}{\partial l}\right)_{T,p} = \left(\frac{\partial f}{\partial T}\right)_{p,l}$$

$$\left(\frac{\partial S}{\partial l}\right)_{T,p} = -\frac{\partial}{\partial T}\left(aT(l-l_0)\right)$$

$$= -a(l-l_0)$$

$$S(l) = \int_{l_0}^{l} -a(l-l_0)dl$$

$$S(l) = -\frac{a(l-l_0)^2}{2}$$

So the entropy is proportional to the square of the extension distance.

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$= TdS + Vdp + fdl$$

$$\left(\frac{dH}{dl}\right)_{T,p} = T\left(\frac{dS}{dl}\right)_{T,p} + f$$

$$= T(-a(l-l_0)) + aT(l-l_0)$$

$$= 0$$

So *H* is constant for all extensions *l*.

b) Since we are told that it is an adiabatic process ($\delta q=0$, so $dU=\delta w=fdl$), we know that we need to start with the expression for internal energy *U*. We also know that by definition, for constant volume $dU=C_v dT$.

$$dU = fdl$$

$$C_v dT = aT(l-l_0)dl$$

$$\frac{C_v}{T}dT = a(l-l_0)dl$$

$$\int_{T_1}^{T_2}\frac{C_v}{T}dT = \int_{l_0}^{l} a(l-l_0)dl$$

$$C_v \ln\left(\frac{T_2}{T_1}\right) = \frac{a(l-l_0)^2}{2}$$

$$\frac{T_2}{T_1} = \exp\left[\frac{a(l-l_0)^2}{2C_v}\right]$$