

BE.011/2.772  
Problem Set 5  
Due March 17, 2004

Dill 9.1, 9.3, 9.8 and 9.10

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9.3 We are given that  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ , and we are asked to show that this implies that  $C_V = \left(\frac{\partial U}{\partial T}\right)_V$  is not a function of  $V$ . For this, we need only prove that  $\frac{\partial C_V}{\partial V} = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V = 0$ . But we know that we can permute the order of the derivatives, so we get that  $\frac{\partial C_V}{\partial V} = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T = \frac{\partial}{\partial T}(0) = 0$ . 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  $\left(\frac{\partial f}{\partial p_0}\right)_{E,S}$  rather than  $\left(\frac{\partial p_0}{\partial f}\right)_{E,T}$  which we want. We need to first transform our equation to a new energy variable  $X(T,f,E)$ .

$$\begin{aligned}dU &= TdS + fdl + Edp_0 \\X &= U - TS - fl - Ep_0 \\dX &= SdT - ldf - p_0dE\end{aligned}$$

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

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

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

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.

$$\begin{aligned}G &= H - TS = U + pV - TS \\dG &= dU + pdV + Vdp - TdS - SdT \\&= -SdT + Vdp + fdl\end{aligned}$$

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

$$\begin{aligned}
\left(\frac{\partial^2 G}{\partial l \partial T}\right) &= \left(\frac{\partial^2 G}{\partial T \partial l}\right) \\
\frac{\partial}{\partial l} \left(\frac{\partial G}{\partial T}\right)_{l,p} &= \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial l}\right)_{T,p} \\
-\left(\frac{\partial S}{\partial l}\right)_{T,p} &= \left(\frac{\partial f}{\partial T}\right)_{p,l} \\
\left(\frac{\partial S}{\partial l}\right)_{T,p} &= -\frac{\partial}{\partial T} (aT(l-l_0)) \\
&= -a(l-l_0) \\
S(l) &= \int_{l_0}^l -a(l-l_0) dl \\
S(l) &= -\frac{a(l-l_0)^2}{2}
\end{aligned}$$

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

$$\begin{aligned}
H &= U + pV \\
dH &= dU + pdV + Vdp \\
&= TdS + Vdp + fdl \\
\left(\frac{dH}{dl}\right)_{T,p} &= T\left(\frac{dS}{dl}\right)_{T,p} + f \\
&= T(-a(l-l_0)) + aT(l-l_0) \\
&= 0
\end{aligned}$$

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  $dU=C_v dT$ .

$$\begin{aligned}
dU &= fdl \\
C_v dT &= aT(l-l_0)dl \\
\frac{C_v}{T} dT &= a(l-l_0)dl \\
\int_{T_1}^{T_2} \frac{C_v}{T} dT &= \int_{l_0}^l a(l-l_0)dl \\
C_v \ln\left(\frac{T_2}{T_1}\right) &= \frac{a(l-l_0)^2}{2} \\
\frac{T_2}{T_1} &= \exp\left[\frac{a(l-l_0)^2}{2C_v}\right]
\end{aligned}$$