5500 Problem Set 1

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September 9, 2020

Question I.

Find (and memorize) the natural variables, expressions of certain thermodynamic parameters as derivatives of the potentials, and the Maxwell relations, for enthalpy $H = U + pV$ and Gibbs free energy $G = U - TS + pV$.

$$\begin{aligned}
H &= U + pV \\
\mathrm{d}H &= \mathrm{d}U + \mathrm{d}(pV) \\
\mathrm{d}U &= \mathrm{d}Q - p\,\mathrm{d}V \\
\mathrm{d}H &= \mathrm{d}Q - p\,\mathrm{d}V + p\,\mathrm{d}V + V\,\mathrm{d}p \\
&= \mathrm{d}Q + V\,\mathrm{d}p
\end{aligned}$$

In a reversible process:

$$\begin{aligned}
\mathrm{d}Q &= T\,\mathrm{d}S \\
\mathrm{d}H &= T\,\mathrm{d}S + V\,\mathrm{d}p
\end{aligned}$$

So H has natural variables S and p. For Gibbs free energy we see

$$\begin{aligned}
G &= U - TS + pV \\
\mathrm{d}G &= T\,\mathrm{d}S - p\,\mathrm{d}V - \mathrm{d}TS + \mathrm{d}pV \\
&= T\,\mathrm{d}S - p\,\mathrm{d}V - T\,\mathrm{d}S - S\,\mathrm{d}T + p\,\mathrm{d}V + V\,\mathrm{d}p \\
&= -S\,\mathrm{d}T + V\,\mathrm{d}p
\end{aligned}$$

So G has natural variables T and p. We find the Maxwell relations:

$$\begin{aligned}
\left(\frac{\partial H}{\partial S}\right)_p &= T \\
\left(\frac{\partial H}{\partial p}\right)_S &= V \\
\left(\frac{\partial G}{\partial T}\right)_p &= -S \\
\left(\frac{\partial G}{\partial p}\right)_T &= V
\end{aligned}$$

Question II.

As customary, let's seriously cut corners and write the first law for a magnetic system as $dU = T\,\mathrm{d}S + B\,\mathrm{d}M$, where, in fact, M is the total magnetic moment and B means H. Show that for a magnetic substance obeying Curie's law $M = CB/T$, with C being a constant, internal energy only depends on temperature. You might be best off thinking about U as a function of T and M.

For a system obeying Curies law, we have:

$$\begin{aligned} M &= \frac{CB}{T} \\ \mathrm{d}M &= CB\frac{1}{T^2}\,\mathrm{d}T \\ \mathrm{d}U &= T\,\mathrm{d}S - CB^2\frac{1}{T^2}\,\mathrm{d}M \end{aligned}$$

We can implement the Helmholtz free energy and get the Maxwell relations

$$\begin{aligned} \mathrm{d}F &= \mathrm{d}U - \mathrm{d}TS \\ &= T\,\mathrm{d}S - \mathrm{d}T\,S - T\,\mathrm{d}S - CB^2\frac{1}{T^2}\,\mathrm{d}T \\ &= -\,\mathrm{d}T\,S - CB^2\frac{1}{T^2}\,\mathrm{d}T \\ \left(\frac{\partial F}{\partial T}\right)_B &= -S \end{aligned}$$

It follows from these that

$$U = U(T)$$

If B is constant.

Question III.

How hot does air get in the pump when you try to put twice the atmospheric pressure in a bicycle tube at the ambient temperature of 20°C? Hints for beginners: Assume that the compression is reversible and takes place without exchange of heat with the environment. Air is predominantly diatomic molecules.

For an adiabatic process we know:

$$
\begin{aligned}
pV^{\gamma} &= C \\
pV &= nRT \\
V &= \frac{nRT}{V} \\
p\left(\frac{nRT}{V}\right)^{\gamma} &= C \\
p^{1-\gamma}T^{\gamma} &= C \\
p_1^{1-\gamma}T_1^{\gamma} &= p_2^{1-\gamma}T_2^{\gamma} \\
T_2 &= T_1\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \\
&= 2^{\left(\frac{\frac{5}{2}-1}{\frac{5}{2}}\right)}T_1 \\
&= 2^{\frac{3}{5}}T_1 \\
&= 303.6 \text{ K}
\end{aligned}
$$

Question IV.

Electromagnetic radiation in a cavity, in equilibrium with the walls at the temperature T, is called blackbody radiation. It is known that (i) energy density (energy per unit volume) is some function $e(T)$ of temperature alone, and that (ii) the pressure that the radiation exerts on the walls is $p = \frac{1}{3}e(T)$. Find the temperature dependence of U, p and S.

Since $e(T)$ is an energy density we know

$$
\begin{aligned}
p &= \frac{1}{3}e(T) \\
\mathrm{d}U &= T\,\mathrm{d}S - p\,\mathrm{d}V \\
U &= e(T)V
\end{aligned}
$$

We also know the following Maxwell relation which gives us

$$
\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial S}{\partial V}\right)_V \\
\left(\frac{\partial U}{\partial V}\right)_T &= e(T)\left(\frac{\partial V}{\partial V}\right)_T \\
&= e(T)
\end{aligned}
$$

We also have

$$\begin{aligned}
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p \\
e(T) &= \frac{T}{3}\left(\frac{\partial e(T)}{\partial T}\right)_V - \frac{e(T)}{3}
\end{aligned}$$

This goes to

$$\begin{aligned}
\frac{\mathrm{d}e(T)}{4e(T)} &= \frac{\mathrm{d}T}{T} \\
e(T) &\propto T^4
\end{aligned}$$

The desired relations follow directly.