Thermodynamics HW #9

Due October 28

1. Schroeder 5.26

   Solution:

   Consider the conversion of graphite to diamond when the material is in contact with a temperature and pressure reservoir.

   The entropy is equal to the sum of the material entropy S_C (C for carbon) and reservoir entropy S_R:

   $$S = S_C + S_R$$

   In the conversion of some small amount dN of graphite to diamond there will be some exchange of energy dU_R and volume dV_R with the reservoir, so we get an entropy change in the reservoir given by

   $$\begin{aligned} dS_R &= \left(\frac{\partial S_R}{\partial U_R}\right)_{V_R,N_R} dU_R + \left(\frac{\partial S_R}{\partial V_R}\right)_{E_R,S_R} dV_R \\ &= \frac{dU_R + PdV_R}{T} \end{aligned}$$

   where T and P are the temperature and pressure of the reservoir. The change dV_R of the reservoir volume should be *opposite* that of the material, so if the material *shrinks*, as it does in the conversion of graphite to diamond, then the reservoir entropy accordingly grows. At high enough pressures then this increase in reservoir entropy can overcome the negative change in material entropy.

2. Schroeder 5.38

   Replace the first two sentences with,"Use Figure 5.17 to estimate the difference in entropy between graphite and diamond at 500K." Answer the other two questions as they are.

   Solution:

   By my eyes I see a slope in the graph of $\frac{60\text{kbar}}{2000\text{K}}$. By equation (5.46) and the volume difference given in the text of $\Delta V = 1.9 \cdot 10^{-6}\text{m}^3$ we then get an entropy difference ΔS of

   $$\Delta S = 5.8\text{J/K}$$

3. Schroeder 5.41

   Solution:

Assume that the vapor and liquid are in equilibrium at a temperature T and total pressure P, and at this T and P the water vapor is at a pressure P_v.

Since the vapor and liquid phases are free to exchange heat and particles, the two phases must have equal chemical potentials:

$$\mu_v(P_v) = \mu_g(P)$$

The chemical potential is also a function of the temperature T, but we omit as a function argument it since it remains constant for all future processes considered.

If we then increase the total pressure by some small amount dP, then in order to remain in equilibrium the vapor pressure must adjust by amount dP_v so that

$$\mu_v(P_v + dP_v) = \mu_l(P + dP)$$

Since the changes are small we can Taylor expand, giving:

$$\mu_v(P_v) + \frac{d\mu_v}{dP_v}dP_v = \mu_l(P) + \frac{d\mu_l}{dP}dP$$

From equation (5.40) we have

$$\frac{d\mu_v}{dP_v} = \frac{kT}{P_v} = \frac{V_v}{N_v} = \rho_v^{-1}(P_v)$$

where ρ_v is the density of the vapor and in the second step we use the ideal gas law.

Further we find

$$\begin{aligned}
&\frac{d\mu_l}{dP} \\
&\quad = \left(\frac{\partial}{\partial P}\frac{N\mu_l}{N}\right)_{T,N} \\
&\quad = \frac{1}{N_l}\left(\frac{\partial}{\partial P}N_l\mu_l\right)_{T,N_l} \\
(a) &\quad = \frac{1}{N_l}\left(\frac{\partial}{\partial P}G_l\right)_{T,N_l} \\
(b) &\quad = \frac{V_l}{N_l} = \rho_l^{-1}
\end{aligned}$$

where in line (a) we use the equation (5.35) and in line (b) we use equation (5.41) and ρ_l is the density of the liquid. Again there is a bit of subtlety with how I've maneuvered the partial derivatives here, so make sure the above is clear to you.

Finally then we have

$$\rho_v^{-1}(P_v)dP_v = \frac{kT}{P_v}dP_v = kTd\ln P_v = \rho_l^{-1}dP$$

integrating both sides we get

$$P_v(P) = P_v^o e^{\frac{P-P_o}{kT}/\rho_l} \equiv P_v^o e^{\frac{\rho(P)\tilde{-}\rho(P_o)}{\rho_l}}$$

where at some total pressure P_o we have a vapor pressure P_v^o. We've denoted $\rho(P)$ as the density of a gas at pressure P. Cast in these terms it is clear that the vapor pressure P_v changes very little with changes in pressure because liquids are typically much denser than gases. The exponent in the above equation for any gas pressure P then will be small so that $P_v(P) \approx P_v^o$. There are rare though notable exceptions to this rule. For a temperature and pressure approaching a critical point (see figure 5.11 so an illustration for water) the molar volumes of the vapor and liquid phases converge. In this case small changes in pressure P can create significant changes in the vapor pressure.

4. (a) Suppose we have a system S in contact with a reservoir R and that they can exchange not only energy but also volume. Consider two micro-states of the system S, one with energy E_1 and volume V_2 and the other with energy E_2 and volume V_2. Show that the relative probabilities $\frac{p_2}{p_1}$ of finding the system in second microstate vs. the first is given by

$$\frac{p_2}{p_1} = e^{-\frac{(E_2-E_1)+P(V_2-V_1)}{kT}}$$

where T and P are the temperature and pressure of the reservoir, respectively.

(b) Now suppose that the reservoir can exchange particles with the system in addition to energy and volume. Suppose that the first microstate has energy, volume, and particle number E_1, V_1, N_1 and likewise for the second microstate. Find their relative probabilities $\frac{p_2}{p_1}$ in this case.

Solution:

The number of microstates of the collective system $S + R$ with S in a given particular microstate is Ω_R, the number of microstates the *reservoir* has when the system S is in the given microstate.

Let E_T, V_T, and N_T be the total energy, volume, and particle number shared between the two systems. Then we get $E_T - E_n$, $V_T - V_n$, and $N_T - N_n$ is the reservoir energy, volume, and particle number when the system is in the n^{th} microstate, where $n = 1, 2$.

From the definition of the reservoir entropy $S_R(E_R, V_R, N_R)$ we have then that

$$\Omega_R(E_T - E_n, V_T - V_n, N_T - N_n) = e^{\frac{S_R(E_T - E_n, V_T - V_n, N_T - N_n)}{k}}$$

since the reservoir is presumably much larger than the system, and E, V, and N are all extensive parameters, then we are justified in approximating the entropy using a Taylor expansion

$$\begin{aligned}
&S_R(E_T - E_n, V_T - V_n, N_T - N_n) \\
\approx &S_R(E_T, V_T, N_T) \\
&+ \left(\frac{\partial S_R}{\partial E_R}\right)_{V_R, N_R} (E_T, V_T, N_T) \cdot (-E_n) \\
&+ \left(\frac{\partial S_R}{\partial V_R}\right)_{E_R, N_R} (E_T, V_T, N_T) \cdot (-V_n) \\
&+ \left(\frac{\partial S_R}{\partial N_R}\right)_{E_R, V_R} (E_T, V_T, N_T) \cdot (-N_n) \\
= &S_R(E_T, V_T, N_T) - \left(\frac{E_n}{T} + \frac{PV_n}{T} - \frac{\mu N_n}{T}\right)
\end{aligned}$$

Where T, P, and μ are the temperature, pressure, and chemical potential of the reservoir when it has an energy, volume, and particle number E_T, V_T, and N_T. The critical assumption here is that the reservoir is so large than its temperature, pressure, and chemical potential varies negligibly from these values for any conceivable transfer of energy E_n, volume V_n, or particle number N_n to the system, so they can be assumed fixed.

Dividing then the reservoir multiplicities when the system S is in states 1 and 2 we find

$$\begin{aligned}\frac{p_2}{p_1} &= \frac{e^{\frac{S_R(E_T,V_T,N_T)-\left(\frac{E_n}{T}+\frac{PV_n}{T}-\frac{\mu N_n}{T}\right)}{k}}}{e^{\frac{S_R(E_T,V_T,N_T)-\left(\frac{E_n}{T}+\frac{PV_n}{T}-\frac{\mu N_n}{T}\right)}{k}}} \\ &= e^{-\frac{(E_2-E_1+P(V_2-V_1)-\mu(N_2-N_1))}{kT}}\end{aligned}$$