Problem Set #11 Due on Thurs. 19 Apr.: (Continued on reverse side.)

#1(a) Below its triple point (-56.6° C) the vapor pressure of solid carbon dioxide may be approximately expressed by the relation \( \log_{10} p = \frac{-1353}{T} + 9.832 \), where \( p \) is in mmHg (i.e., torr) and \( T \) is the absolute temperature (K). The latent heat of fusion at the triple point is 8647 J/mol. Estimate the vapor pressure of liquid carbon dioxide at 0° C. Given that the latent heat of vaporization decreases with increasing temperature, is your estimated vapor pressure likely to be greater than or less than the actual value? (Note: 760 torr = 1 atm = 1.01325 \times 10^5 Pa)

(b) Show that at the s-l-v triple point of a pure material \( \frac{dp}{dT} \) sub > \( \frac{dp}{dT} \) vap when the latent heat of fusion is >0.

#2 (a) Max Planck, one of the founders of quantum mechanics, also made important contributions to thermodynamics. His equation for the rate of change of the molar latent heat, \( \ell \), of a phase transition with temperature \( T \) along the equilibrium \( p-T \) curve can be written as

\[
\frac{d\ell}{dT} = \Delta c_p + \frac{\ell}{T} - \ell \frac{\partial \ln v}{\partial T} \bigg|_p,
\]

where \( c_p \) is a molar heat capacity at constant pressure and \( v \) is a molar volume. Derive this result by taking the total (not partial) temperature derivative of \( \ell \), defined as \( \ell = \Delta h = T\Delta s \), where \( h \) and \( s \) are the molar enthalpy and entropy, respectively.

(b) Reif 8.4 (Look at He phase diagram in class notes for help. See pages 11 and 13 of L 20)

#3 At 298.15 K and 1 atm, the density of diamond is 3.52 g/cm³ and that of graphite is 2.25 g/cm³. At this temperature and pressure, the Gibbs molar free energy of diamond is 2.87 kJ/mol higher than that of graphite. What is the stable phase of carbon under these conditions? At what pressure will diamond and graphite be in equilibrium at 298.15 K?

See other side for the rest of this assignment.
#4 The freezing point of water decreases with pressure until $p = 0.22$ GPa. At this solid-solid-liquid triple point a new phase of ice, known as Ice-III, appears, and the freezing point of water now begins to increase with pressure. At 273.15 K, the latent heat of melting is 333 J/g, and the densities of Ice-I and liquid water are $\rho_I = 0.917$ g/cm$^3$ and $\rho_{liq} = 1$ g/cm$^3$, respectively. Assuming these values to be constants, estimate the temperature of the high pressure triple point. This is the lowest temperature at which liquid water is a stable equilibrium phase. Draw a qualitative sketch of this solid-liquid region on a $p-T$ phase diagram. Assume that $\rho_{III} > \rho_I$ and $\rho_{III} > \rho_{liq}$ and include the Ice-III–Ice-I and Ice-III–liquid phase equilibrium lines on your diagram. The latent heat for the transition Ice-I $\rightarrow$ Ice-III is positive and small.

#5 Evaluate the exact, general relation for $c_p - c_v$ derived in Lecture 15 (Ch. 5) for a van der Waals fluid or derive this result directly from the entropy expression in part (b) of Problem 2, HW#10. Express your answer in terms of $\nu'$ and $T'$, where these variables are defined in Reif Problem 5.19 on p. 198. See the notes for Lecture 20 for the solution to 5.19. You may find it simpler to work with the reduced, dimensionless equation of state provided there. Use your result to show that, along the critical isochore ($\nu' = 1$), $c_p$ diverges as $(T' - 1)^{-1}$ as $T'$ approaches 1 from above.

#6 A liquid is in equilibrium with its own vapor at some temperature $T$ and pressure $p$. The latent heat of vaporization per mole of liquid is $\ell_v$ (>0). Suppose 3 moles of vapor are quasistatically (reversibly) converted to liquid at constant $T$ and $p$.

(a) For this process, what are the values of the following thermodynamic quantities $\Delta G$, $\Delta H$, $\Delta S$, $\Delta V$, $\Delta E$, $\Delta F$, $Q$, and $W$? Assume that the molar volume of the liquid is much smaller than the molar volume of the vapor, $v_l << v_v$. Express your answers in terms of $R$, $T$, $p$, and $\ell_v$.

(b) What is the direction of heat transfer for this process?

(c) What is the minimum amount of work that must be performed on the system to return it to its initial state?