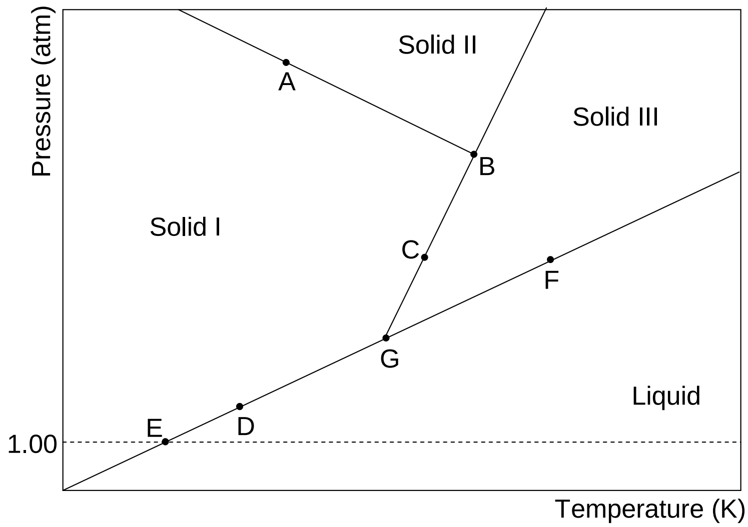
Quiz 5
CHEM 323
Fall 2008

Name: ____

1. (8 Points) A portion of the phase diagram for a certain pure substance is shown below. Write the letter from the diagram in the blank next to the item in the following list that it matches. Note that some letters may be used more than once, or not at all. If a particular item is not shown in the given portion of the phase diagram, write "Not Shown" in the space.



a. Normal melting point **E** *(occurs at 1.00 atm of pressure)*

b. Standard melting point **Not Shown** *(at 1.00 bar of pressure, which is less than 1 atm)*

c. Critical point **Not Shown** *(point where the liquid-gas line ends)*

d. Triple point **B, G** *(any point on a phase diagram where three phases coexist)*

2. (3 Points) What can you conclude about the density of solid phase II relative to that of solid phase I?

The line that separates phase I from phase II has a positive slope and therefore the derivative $\frac{dp}{dT}$ is positive. Since $\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$, $\frac{\Delta_{trs}S}{\Delta_{trs}V}$ must also be positive, which can happen only if both $\Delta_{trs}S$ and $\Delta_{trs}V$ have the same sign. We do not know either of these for the transition between the two solid phases, and so we can't say anything about the density.

One might expect that $\Delta_{trs}V$ to be negative because elevated pressure is required to bring about the phase change. However, it is possible that by increasing the pressure on solid I *that repulsive interactions between the particles become dominant. The phase change could be then be the result of the solid adopting a different structure that makes the particles be farther apart and hence increases the volume ($\Delta_{trs}V > 0$).*

3. (8 Points) At 1.00 bar of pressure ^{4}He boils at 4.22 K with $\Delta_{vap}H^0$ equal to 0.0840 kJ/mole. What pressure, in bar, is required to have ^{4}He boil at 1.50 K?

Integrate the Clausius-Clapeyron equation, $\frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$ **, assuming that** $\Delta_{vap}H^0$ **is independent of** T**.**

$$d \ln p = \frac{\Delta_{vap}H}{RT^2} dT = \left(\frac{\Delta_{vap}H}{R}\right)\frac{1}{T^2} dT$$

$$\int_{p_1}^{p_2} d \ln p = \left(\frac{\Delta_{vap}H}{R}\right)\int_{T_1}^{T_2} \frac{1}{T^2} dT$$

$$\ln(p_2) - \ln(p_1) = -\left(\frac{\Delta_{vap}H}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{p_2}{p_1}\right) = -\left(\frac{\Delta_{vap}H}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Let p_1 = 1.00 bar **and** T_1 = 4.22 K **and** T_2 = 1.50 K**.**

$$\ln\left(\frac{p_2}{1.00\ \text{bar}}\right) = -\left(\frac{0.0840x10^3\ \frac{\text{J}}{\text{mole}}}{8.31447\ \frac{\text{J}}{\text{K}\cdot\text{mole}}}\right)\left(\frac{1}{1.50\ \text{K}} - \frac{1}{4.22\ \text{K}}\right)$$

$$\ln\left(\frac{p_2}{1.00\ \text{bar}}\right) = -(10.1_0\ \text{K})(0.666_6 - 0.236_9\ \text{K}^{-1}) = -(10.1_0\ \text{K})(0.429_7\ \text{K}^{-1}) = -4.33_9$$

$$p_2 = (1.00\ \text{bar})(e^{-4.33_9}) = 0.013\ \text{bar}$$

The pressure must be dropped to 0.013 bar to lower the boiling point of He to 1.50 K.

FYI, this is a common method to achieve temperatures near absolute zero, but is limited, of course, by the efficiency of your pump.

4. (5 Points) Calculate the change in the molar Gibbs energy, G_m, for ice at -10.0 °C (density equals 917.0 $kg \cdot m^{-3}$) when the pressure is raised from 1.0 bar to 2.0 bar. The molar mass of water is 18.016 g/mole.

We can either start with the equation $\left(\frac{\partial G}{\partial p}\right)_T = V$ **and integrate assuming that** V **is independent of** p**, which is reasonable for a solid, or we can start with the equation** $G_m(p_f) = G_m(p_i) + V_m \Delta p$ **, which is the result of this integration. The change in** G_m **due to a change in** p **can then be written as** $\Delta G_m(p) = V_m \Delta p$ **.**

We know that Δp = +1.0 bar **and need to find** V_m**, which may be calculated from the density as follows.**

$$V_m = \left(\frac{1\,\text{m}^3}{917.0\,\text{kg}}\right)\left(\frac{1\,\text{kg}}{1000\,\text{g}}\right)\left(\frac{18.016\,\text{g}}{1\,\text{mole}}\right) = 1.964_6\,x10^5\ \text{m}^3 \cdot \text{mole}^{-1}$$

Substituting into the expression for ΔG_m **gives**

$$\Delta G_m(p) = \left(1.964_6\,x10^{-5}\ \text{m}^3\right)\left(+1.0\ \text{bar}\right)\left(\frac{10^5\ \text{Pa}}{1\,\text{bar}}\right)\left(\frac{1\,\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}}{1\,\text{Pa}}\right)\left(\frac{1\,\text{J}}{1\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}}\right)$$

$$\Delta G_m(p) = +2.0\ \text{J}$$

For this process, ice's molar Gibbs energy only increases by 2.0 J.