Chemistry 236
Triple Point Study Problems -- Answers

1. c   **2.** c   **4.** $\Delta H_{m,fus} = \Delta H_{m,sub} - \Delta H_{m,vap} = 6.859$ kJ/mol.

3. The vapor pressure is determined by the <u>coldest spot</u> in the apparatus that is exposed to the vapor. Thus, heating the sample cell would lead to condensation of liquid in the vacuum line and pressure gage, and the vapor P would be determined by the cold spot in the line, wherever that happened to be. To measure vapor pressures above room T with this apparatus would require heating the line and gage to a temperature above that of the sample cell.

6. (1)   295 Torr   (2)   117 Torr

7. One can find tabulated values (*e.g.*, on p. 960 of Levine) for $H_2O(g)$ and $H_2O(l)$, but these are for the substances <u>in their standard states at 25°C</u>, namely pure liquid water at $P = 1$ bar and $H_2O(g)$ in the ideal gas standard state. As we will see later in Chemistry 231, the ideal-gas approximation will have little effect on our results, but the T of 25°C is far enough from the triple point to introduce significant differences. To convert from 25°C to 0.01°C, we need the heat capacities of liquid and gaseous water. Then use Eqns. (5.18) and (5.19) of Levine (p. 151) to carry out the conversion.

8. From the CRC Handbook in the lab, the vapor pressures of water at 0°C and 5°C are 0.61129 and 0.87260 kPa, respectively. Using Eqn. (6) or (7), these values yield $\Delta H_{m,vap} = 44.966$ kJ/mol. For comparison, the CRC Handbook also gives values for $\Delta H_{m,vap}$ at 0°C and 25°C (45.054 and 43.990 kJ/mol, respectively). If we assume our just-calculated value is for the middle T, 2.5°C, then we can compare it with the tabulated values by linearly interpolating on the latter. Interpolating $^1/_{10}$ of the way between 0°C and 25°C yields 44.948 kJ/mol, which is within 0.02 kJ/mol of our vapor-P-based value and probably within experimental error of both determinations.

        From p. 961 of Levine, the calculated $\Delta H°$ for $l \rightarrow g$ is 44.012 kJ/mol, which is 0.022 kJ/mol larger than the previously mentioned tabulated value for $\Delta H_{m,vap}$ at 25°C. This difference is probably partly a consequence of the ideal gas assumption behind the calculated value based on the Appendix in Levine and partly a reflection of unreported experimental uncertainty in results from different sources. Using the $C_{P,m}°$ values given in the Appendix and Eq. (5.19) of Levine, we obtain 44.951 kJ/mol at 2.5°C. This value is in close agreement with the two values determined just above, being closer to the interpolated result. Neglect of T-dependence in both $C_{P,m}°$ values, however, is still a source of error (but evidently not a large one).

9. Let $\Delta H_m(T) = \Delta H_{m,0} + C_{p,0}(T - T_0) \equiv a + bT$, w/ $a = \Delta H_{m,0} - C_{p,0}T_0$ and $b = C_{p,0}$. Substituting into Eq. (4), separating variables, and integrating both sides from T_0 to T yields $R \ln(P/P_0) = b \ln(T/T_0) + a(1/T_0 - 1/T)$. This is valid for <u>any</u> T_0, and $\Delta H_{m,0}$ and $C_{p,0}$ are the values of these quantities at that T_0.

10. (a)   Yes; $\partial d/\partial d > 1$.

   (b)   0.070(10)°C [$= a$ and σ_a]

   (c)   0.0701632, 4.290986e–05, –0.000525418, 5.87063e–06