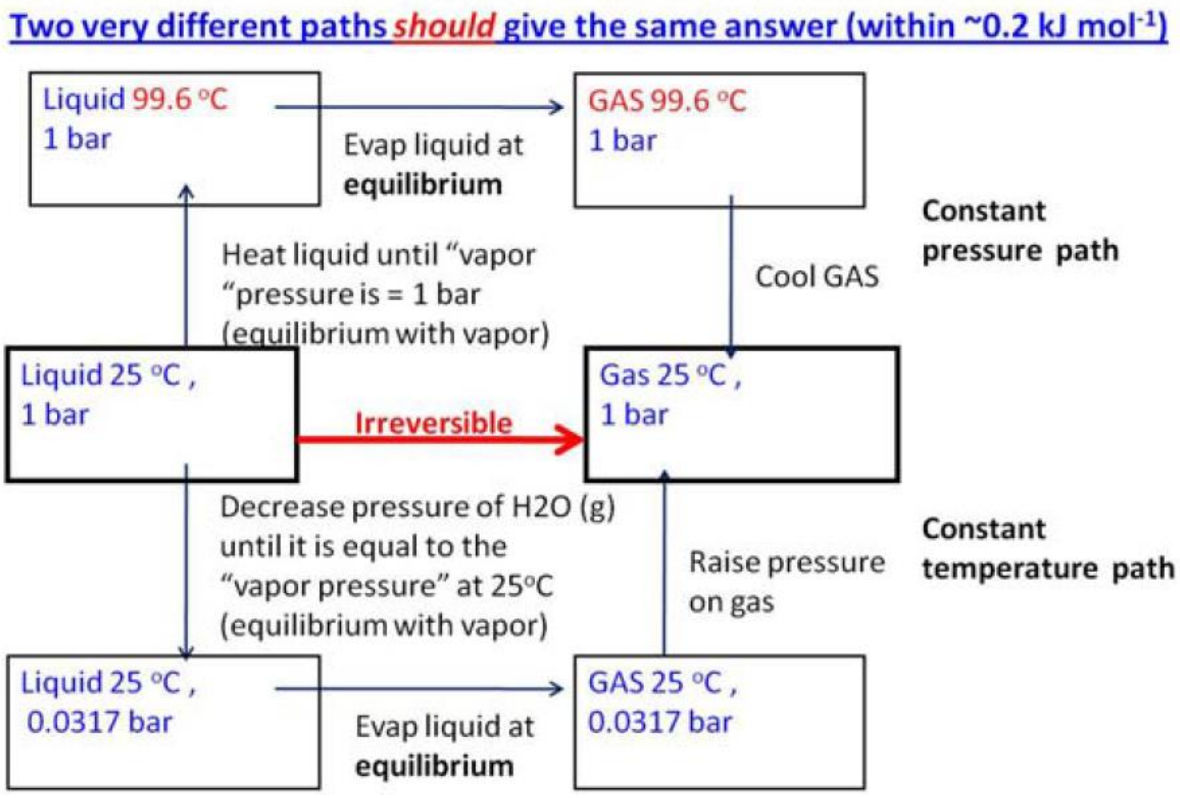
CHMY 361
September 21, 2017
Homework Assignment #2. Due Fri, Sept 29.
Chapter 3, Problems: 4, 24, 26, and Supplemental Problems S1, S2, S3 and S4 below. S4 is quite similar to problem 27.

Supplemental Problems for Chapter 3.



3.S1 <u>**IMPORTANT NOTE:**</u> The pressures in the Figure above are for the **partial pressure of H2O(g)**. There is no air involved in this system.

(a) ΔH^o and ΔS^o for the process $H_2O(l)$--->$H_2O(g)$ at 1 bar partial pressure of H2O(g) at 25°C tabulated in Table A.5 are not measureable (not at equilibrium). Explain the difficulties in measuring the q for this process under these conditions.

(b) Using data in Table 2.2 and illustrated in the figure above, and making reasonable approximations, calculate ΔS^o, ΔS_{surr}, and ΔS_{univ} for the reversible, constant pressure path between the two state of (a) involving evaporation at 99.6 °C.
(c) Do the same for the constant temperature path.

(d) Compare the values from (b) and (c) with the values obtained from Table A.5 for the process in (a).

(e) Calculate ΔS_{surr}, and ΔS_{univ} for the irreversible path (process (a)) of vaporization at 25° C and 1 bar, and tell whether it is expected to be spontaneous, impossible, or at equilibrium.

3.S2. Consider a system consisting of a **closed** bottle of honey (super-cooled glucose solution) kept at 298 K in a thermostated room. Over time crystals of glucose will **spontaneously** form. Tell whether ΔU, ΔH, q, w, ΔS, ΔS_{surr} and ΔS_{univ} are positive , zero, or negative for this process. Justify each of your answers. Pressure is constant. Assume the volume change is negligible, and there is **no** non-pV (useful) work.

3.S3. Consider two crystal forms of a certain substance with molecular weight = 50 g/mol. At 298K and 1 bar, the following values are tabulated:

	$\Delta_f G^0$ (kJmol^{-1})	density (g/ml)
Form 1	-100.0	2.00
Form 2	-150.0	1.00

(a) Which form is most stable at 298 K?

(b) At what applied pressure in bars will the two forms be in equilibrium at 298 K?

3.S4. Given that the ***generic*** form state variable B = a function of state variables C and D, i.e., B=f(C,D), implies quite ***generally*** that

$$dB = \left(\frac{\partial B}{\partial D}\right)_C dD + \left(\frac{\partial B}{\partial C}\right)_D dC$$

and if it is ***<u>also</u>*** true that $dB = F\,dD + E\,dC$ (such relationships abound in thermodynamics), use the examples on pp 87-90 to answer the following:

(a)Write the obvious expressions for F and E as partial derivatives of A. (This can be done by ***inspection***!)

(b) Using the applicable Maxwell relation, $\left(\frac{\partial E}{\partial D}\right)_C = ?$ (also quickly done by ***inspection***!)

Note that A, B, C, D, and E can be anything in any field of endeavor that have the attributes of state functions. Also, it is ***completely unnecessary*** to learn and use the "Thermodynamic Square" (pp 91-92), and not helpful for this problem. This problem, however, applies directly to all the analogous thermodynamic relations on pages 87-92.