

CHMY 361

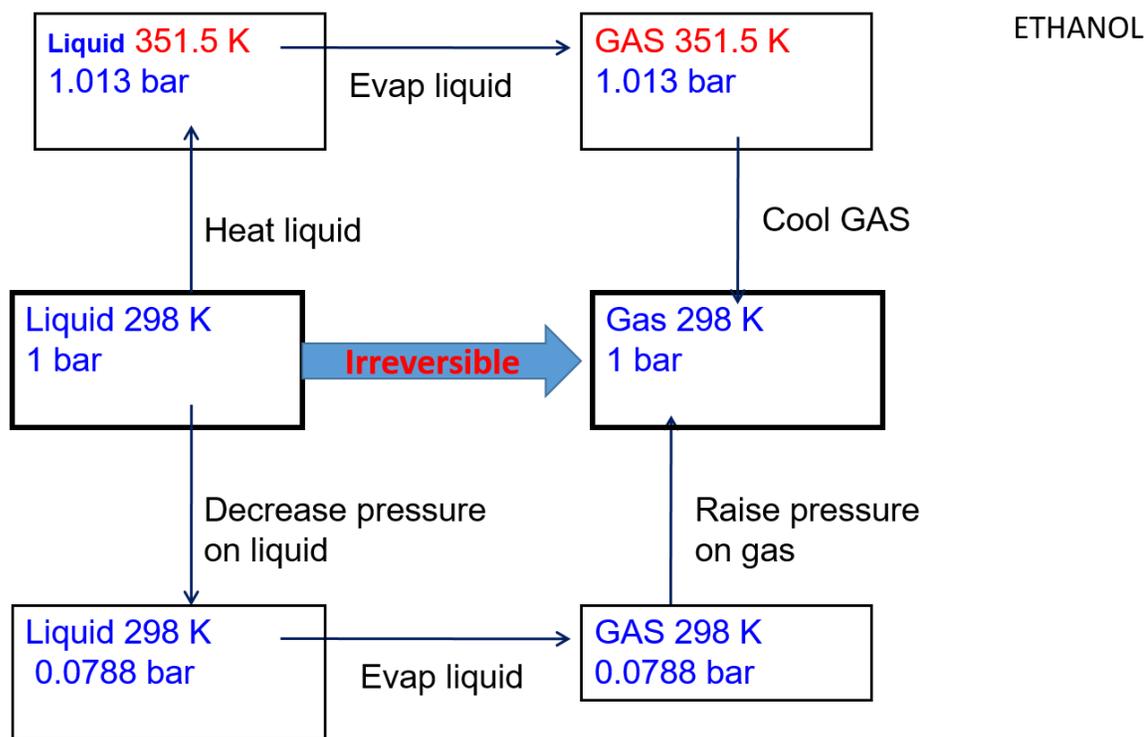
September 22, 2018

Homework Assignment #2. Due Fri, Sept 28.

Chapter 3, Problems: 4, 26, and Supplemental Problems S1, S2, S3 and S4 below. S4 is quite similar to problem 27.

Supplemental Problems for Chapter 3.

**Two very different paths should give exactly the same answer for ethanol**



Path does not matter: **H** is a STATE FUNCTION

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

Tabulated Data from the Internet you will need:

Ethanol(g) :  $\Delta_f H^0 = -235.3$  kJ/mol;  $C_{p,m} = 78.28$  J/(mol K);  $S^0$

Ethanol(l) :  $\Delta_f H^0 = -277.38$  kJ/mol  $C_{p,m} = 112.4$  J/(mol K);  $S^0$

(a)  $\Delta H^0$  and  $\Delta S^0$  for the process Ethanol(l)--->Ethanol(g) at 1 bar partial pressure of Ethanol(g) at 25°C, are not measurable. Explain the difficulties in measuring the q for this process at 1 bar partial pressure of at 25°C.

(b) Using data above and illustrated in the figure above, and making reasonable approximations, calculate  $\Delta S^\circ$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  for evaporation at 298 K via the reversible, constant pressure path between the two states involving equilibrium evaporation at 351.5 K

(c) Do the same for the constant temperature, low pressure path for evaporation at 298 K

(d) Compare the values from (b) and (c) with the values obtained tabulated above from Wikipedia for the process in (a).

(e) Calculate  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  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 supersaturated salt solution in which some large crystals of the salt begin to grow. The system is thermostated with a temperature bath at 298 K. Tell whether  $\Delta G$ ,  $\Delta U$ ,  $\Delta H$ ,  $q$ ,  $w$ ,  $\Delta S$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{univ}}$  are positive, zero, or negative for the process: Justify each of your answers. Pressure is constant =  $p_{\text{ext}}$ . Assume the volume change is negligible, and there is no non-pV work.

**3.S3.** Consider two crystal forms of a certain substance with molecular weight = **100.0** g/mol. At 298K and 1 bar, the following values are tabulated:

	$\Delta_f G^\circ$ (kJmol <sup>-1</sup> )	density (g/ml)
Form 1	-100.0	2.00
Form 2	-170.0	1.50

(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 for state variable B = a function of state variables D and E, i.e., B=f(D,E)), implies quite *generally* that

$$dB = \left( \frac{\partial B}{\partial D} \right)_E dD + \left( \frac{\partial B}{\partial E} \right)_D dE$$

and if it is also true that  $dB = JdD + KdE$  (such relationships abound in thermodynamics), use the examples on pp 87-90 to answer the following:

(a) Write the obvious expressions for J and K as partial derivatives of B. (This can be done by *inspection!*)

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

Note that B, D, E, J, and K 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.

**Important that you realize that the above is just another way of expressing:**

$$\mathbf{y} = \mathbf{m}\mathbf{x} + \mathbf{b},$$

except this is for a case where y depends on 2 variables,  $x_1$  and  $x_2$  so that we have

$$\mathbf{y} = \mathbf{m}_1\mathbf{x}_1 + \mathbf{m}_2\mathbf{x}_2$$