CHEM352: Physical Chemistry I / Fall 2020
Problem Set III - due 17^{th} of Nov, 5.00 pm

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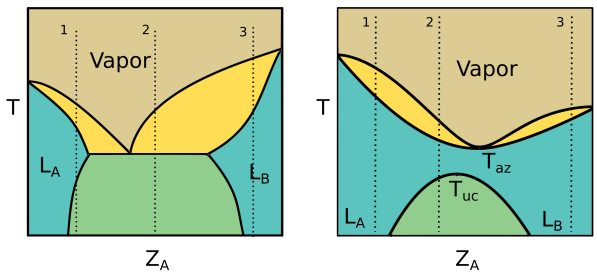
20 points total/2 points per problem

1. Assume ideal solution of benzene and toluene.
   (a) Why would Raoult's Law hold for this solution?
   (b) What's the mixing free energy of 12 g of benzene and 25 g of toluene? What's the entropy of mixing at room temperature?
   (c) Pressures above pure liquids (P^*) of benzene and toluene are equal to 0.128 and 0.038 bars respectively. Calculate the pressure of vapors above the solution in equilibrium. What's the composition of these vapors?

2. (a) The boiling point elevation K_b and freezing point depression constants K_f for carbon disulfide are 3.4 and 2.8 $[K \cdot kg \cdot mol^{-1}]$ respectively. Calculate a change in standard freezing point (161.0 K) and standard boiling point (319.2 K) of 125 g of CS_2 when 2.5 g of substance which has a molar mass of 75 g/mol is dissolved in it. What will be the osmotic pressure pressure of the solution at standard temperature (ρ_{CS_2}=1.26 g/cm^3)? Assume activity coefficient 1.
   (b) Explain on what preperties the freezing point depression constant depends on.

3. Analyze example 9.12 in the book (about a diver) and estimate how many moles of nitrogen would dissolve in his blood at the bottom of Mariana trench. What are your feelings about the poor guy? Draw an illustration of the process.

4. Analyze the 'bunny-ear' and 'beheaded bunny' diagrams below and list all phases present (including an estimate for the composition) and phase transitions that occur (including estimated temperature) when increasing temperature along lines 1, 2 and 3.



5. At 298.15 K, the pKa for formic acid is equal 3.74. Using Debye-Hückel limiting law and Davies equation, calculate the pH in 0.025 m and 1.50 m solutions. Which equation is more applicable to low concentration? Compare the calculated pH values with the situation when $\gamma_{\pm}$ is equal to 1.

6. Calculate the exent of hydrolysis of 0.3 m solution of diethylamine ($pK_a = 10.98$) in (a) pure water and (b) 1 m solution of sodium nitrate. (c) plot the extent of hydrolysis as a function of sodium nitrate concentration.

7. (a) Determine E° for the reaction:

$$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq) \tag{1}$$

   using three and two electron reduction reactions of cobalt cations.
   (b) Determine the activity of $Sn^{4+}(aq)$ in the following reaction at 298.15K at equilibrium:

$$Sn(s) + Sn^{4+}(aq) \rightleftarrows 2Sn^{2+} \tag{2}$$

   when $a_{Sn^{2+}}$ is 0.25.

8. (a) Write the cell reactions, and calculate cell potential and ΔG_R^o at 25^oC of the Fe(s)—$FeSO_4$ (a=0.05) — AgCl (s) — Ag(s)

   (b) Calculate the ΔG_R^o and equilibrium constant of the reduction of the acidic solution of sodium dichromate with molecular hydrogen (gas) at room temperature.

9. (a) K_{sp} for $AgBr$ at 298.15K using the electrochemical cell descibed by:

$$Ag(s)|Ag^+(aq, a_{Ag^+})||Br^-(aq, a_{Br^-})|AgBr(s)|Ag(s) \tag{3}$$

   You can find respective chemical potentials in Table 11.2 in the appendix or use your favorite web-search protocol.

   (b) Standard Calomel (Hg_2Cl_2) Electrode (SCE) is defined by following half-cell reaction:

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq) \tag{4}$$

   Starting from the half-cell of $Hg_2^{2+}(aq) \rightarrow 2Hg(l), E^o = +0.80V$, derive the potential of SCE ($a_{Cl^-} = 1M$) and the electrode immersed in solution of saturated KCl ($a_{Cl^-} = 4.5$M).

10. How does lithium-ion battery work? (Figure + 2 brief paragraphs).