

Homework week 10 (Solubility and complex formation)

In some cases, there are “hints” at the bottom of the problem set. In these cases the word *Hint* is shown after the question. Try struggling with the question for a while before jumping to the hint which, by the way, is often not a “big hint”.

- What is the molar solubility of  $\text{BaSO}_4(\text{s})$  in water?  $K_{\text{sp}} = 4.3 \times 10^{-11}$  (ignore hydrolysis of  $\text{SO}_4$  to form  $\text{HSO}_4^-$ .)
  - Would this solid be more soluble in an acidic or basic solution? Why or why not? *Hint*
  - OK, let's make this a bit more ~~challenging~~ interesting... Give a reasonable estimate of the molar solubility of  $\text{BaSO}_4(\text{s})$  in a solution that is buffered at  $\text{pH} = 2$  (For  $\text{H}_2\text{SO}_4$   $K_{\text{a}1} = \text{Big}$ ;  $K_{\text{a}2} = 1.03 \times 10^{-2}$ ).
- $\text{Ni}(\text{OH})_2(\text{s})$  is minimally soluble in water. ( $K_{\text{sp}} = 6 \times 10^{-16}$ ) To what  $\text{pH}$  would you have to buffer the solution in order to bring  $[\text{Ni}^{2+}]$  to  $1.00 \times 10^{-3} \text{ M}$ ?
- 6.0 g of  $\text{NaCl}$  is added slowly to a 1.0 L solution containing both  $1 \times 10^{-3} \text{ M Ag}^+$  and  $\text{Pb}^{2+}$ . (For  $\text{AgCl}$   $K_{\text{sp}} = 1.8 \times 10^{-10}$ ; for  $\text{PbCl}_2$   $K_{\text{sp}} = 1.7 \times 10^{-5}$ )
  - What will precipitate first as the  $\text{NaCl}$  is added?
  - After all the  $\text{NaCl}$  is added and the system reaches equilibrium, what are the concentrations of all solution species? *Hint*
- It seems peculiar that the solubility of  $\text{PbF}_2$  increases if  $\text{HNO}_3$  is added to the solution, but the addition of this acid to  $\text{PbCl}_2$  has little effect. Why might that be? *Hint*
  - You are initially puzzled and figure that you perhaps need a different acid for the  $\text{PbCl}_2(\text{s})$  so you add  $\text{HCl}$ . **Yikes!** Now, even less  $\text{PbCl}_2$  dissolves than it did in plain water! What is going on!!!
- One form of a chemical *heating pad* consists of a solution of supersaturated sodium acetate ( $\text{CH}_3\text{CO}_2\text{Na}$ ). When a “physical shock” (a small clicker disk) is given the solution it proceeds to equilibrium, precipitates sodium acetate and generates heat.
  - From this information, is the heat of solution for sodium acetate greater than or less than 0?
  - After the pack has reached equilibrium and you wanted to try to rejuvenate it by once again making a supersaturated solution. Would you heat or cool the solution in an attempt to redissolve the solid?
  - A *cold pack* can be made by dissolving solid ammonium nitrate in water. In this case, is the heat of solution for ammonium nitrate greater than or less than 0?
- Copper tetraamine (AKA tetraamminecopper(II)) is a water-soluble complex formed between copper and the ammonia ligand,  $\text{Cu}(\text{NH}_3)_4^{2+}$ . It has step-wise formation constants of  $1 \times 10^4$ ,  $2 \times 10^3$ ,  $5 \times 10^2$  and  $9 \times 10^1$  for  $K_1$  to  $K_4$ , respectively.  $K_f = K_1 K_2 K_3 K_4 = 9 \times 10^{11}$ .
  - Given a solution that is 1.0 F in  $\text{NH}_3$  and  $1 \times 10^{-3} \text{ F}$  in  $\text{Cu}^{2+}$ , calculate the concentration of all copper containing species in the solution. (Ignore the acid/base character of  $\text{NH}_3$ ) *Hint*
  - Let's assume that we have 1.0 g of the relatively insoluble solid,  $\text{CuCO}_3(\text{s})$ , sitting at the bottom of a 1 L beaker of water. (For  $\text{CuCO}_3(\text{s})$   $K_{\text{sp}} = 2.3 \times 10^{-10}$ , i.e., not very soluble... to say the least.) I intend to dissolve this by forming the soluble  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex by adding  $\text{NH}_3$  to the solution. (We're going to neglect any volume change for this problem.) What is  $[\text{NH}_3]$  in the solution once I get all of the  $\text{CuCO}_3(\text{s})$  to dissolve? (Let's only worry about  $K_f$  and assume that only the  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex forms.) *Hint*
- “Austin's alkaline soil can help get the lead out of homegrown veggies” is the title of an Austin American Statesman article back in 2009 ([http://testmygarden.com/austin-tx-soil-testing\\_5\\_1322066470.pdf](http://testmygarden.com/austin-tx-soil-testing_5_1322066470.pdf))

a) Can you explain chemically why this seems like a reasonable statement... or, at least, “seem logical” that we should have less concern than those places with more acidic soils? *Hint*

b) If you lowered the pH of the soil by one pH unit, how much would you increase the mobile  $[\text{Pb}^{2+}]$  ?

8. Scale ( $\text{CaCO}_{3(s)}$ ) precipitates from water, forms on pipes and can severely restrict (or stop!) the flow of water. It is a particular problem in hot water pipes, hot water heaters, boilers and the like both in your home and in industry. Is  $\Delta H >0, =0$  or  $<0$  for the reaction  $\text{Ca}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightarrow \text{CaCO}_{3(s)}$ ?

Any idea of how you might mitigate this problem?

Is this type of temperature dependence that you might typically expect when thinking of the dissolution (or precipitation) of a solid?

==== Spoiler alert: Don't look at hints below until you tried the above on your own =====

*Hints for selected problems:*

- 1b Consider using the exact treatment remembering that you cannot write a charge balance expression because you are in a buffer. Is there anything unique about the solution composition because  $\text{pH} \sim \text{pK}_{a2}$ ? Remember: In a system at equilibrium, all equilibrium constants must be satisfied.
- 3b Be sure to see the final concentrations are not more than you started with!
- 4 Think LeChatlier and the impact (or lack of impact) by added acid.
- 6 a) Think LeChatlier to consider which species dominates, i.e., there is a lot of  $\text{NH}_3$  present relative to the  $\text{Cu}^{2+}$ , yes? Are the Ks for the formation of the complexes large or small?  
b) Step at at time... if all the solid disappears, what is the  $\text{CO}_3^{2-}$  concentration in solution? ... and what would free  $[\text{Cu}^{2+}]$  have to be? Can you guess at how much of the copper from the original  $\text{CuCO}_{3(s)}$  must be tied up in the soluble amine complex? All set now?
- 7 You have to visualize the “soil” as a solution of a given pH with  $\text{Pb}(\text{OH})_{2(s)}$  sitting at the bottom of the beaker. This is not a bad visualization since the plants feed from the water in the soil; and now we simply have to assume that that water and its solutes are in equilibrium with the soil composition.