

# News

- Results on Quiz 4 and HW 2 posted
- Exam 1
  - covers acids and bases and solubility
  - make sure you bring your ptable and your tables of  $K_a$ s and  $K_{sp}$ s
  - usual length
  - nomenclature will be woven into the exam
  - equations provided as usual

# Uses of $K_{sp}$ -beyond simple dissolution

- As the discussion of pption has shown, use of the  $K_{sp}$  extends beyond simply preparing a saturated solution by dissolution of a salt. It is critical to remember that the ion concentrations are only stoichiometrically related if the sat'd solution is prepared by direct dissolution of the salt.
- In general, the generic statement: “For a saturated solution of the salt,  $M_aX_b$ , what would the  $[M^+]$  ( $[X^-]$ ) be if the  $[X^-]$  ( $[M^+]$ ) equals...” describes the general application of  $K_{sp}$  to saturated solutions.
- For a saturated solution of silver bromide, what is the  $[Ag^+]$  if  $[Br^-]=1.3 \times 10^{-3}M$ ?
- A solution of zinc nitrate has  $[Zn^{2+}]=0.025M$ . At what pH would ppt form?

# LeChatelier Effects

- Any equilibrium discussion must include LeChatelier effects. In solubility, these take two forms:
- Chemical processes that decrease the concentration of one of the product ions thereby increasing the solubility. How can this be done?
  1. Adding acid to some salts increases the solubility-explain this in general LeChatelier terms and with also in specific chemical terms
    - ex: carbonates are more soluble in acidic solution
    - ex: the solubility of AgCl is not affected by adding H<sup>+</sup>
  2. Complexation of the cation by a Lewis base
    - Ex: AgCl is soluble in NH<sub>3</sub> solutions
    - $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$  (K<sub>sp</sub>) then  $\text{Ag}^+ + 2\text{NH}_3 \Rightarrow \text{Ag}(\text{NH}_3)_2^+$  (K<sub>f</sub>)
    - what type of compound is Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>
    - your text deals with this quantitatively (ex 16.12 p697). We will not be doing any calculations at this time. The key idea is that the combination of the K<sub>sp</sub> and the K<sub>f</sub> gives K for the process
    - $\text{AgCl} + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^-$   $K = K_f * K_{sp}$
    - What requirements are there for a Lewis bases to increase the solubility of a salt?
  3. Certain hydroxides are amphoteric. That is, they are capable of accepting as well as donating a hydroxide ion. The key example of this behavior is Al<sup>3+</sup>, which, as base is added first ppt and then redissolves due to the formation of Al(OH)<sub>4</sub><sup>-</sup>.

# The Common Ion Effect

- Combining a soluble salt and an insoluble salt which have an ion in common is analogous to mixing a weak and a strong acid. As expected, the presence of the soluble material decreases the solubility of the insoluble salt, just as the strong acid decrease the % ion of the weak acid.
- What is the solubility of CuCl in 0.010M copper(I) nitrate?
- $K_{sp} = [Cu^+] [Cl^-] = 1.7 \times 10^{-7}$
- if  $[Cu^+] = 0.010$  then the  $[Cl^-] = 1.7 \times 10^{-7} / 0.010 = 1.7 \times 10^{-5}$  which would be the molar solubility,  $s$ , of the CuCl
- How does this compare with the molar solubility of CuCl in water?
- What is the solubility of calcium fluoride in 0.050M calcium nitrate?
- $K_{sp} = [Ca^{2+}] [F^-]^2 = 1.5 \times 10^{-10}$
- if  $[Ca^{2+}] = 0.050$  then  $[F^-] = (1.5 \times 10^{-10} / 0.050)^{1/2} = 5.5 \times 10^{-5}$
- Unlike the case of the CuCl, this is not the solubility, but  $2s$ , so  $s = 2.8 \times 10^{-5}$
- $s$  for calcium fluoride in water is  $3.3 \times 10^{-4}$

# How much precipitate?

- If you combine 25mL of 0.01M zinc nitrate with 75mL of 0.020M sodium carbonate, how many grams of ppt form?
- $K_{sp}$  for  $ZnCO_3 = 1.2 \times 10^{-10}$
- $[Zn^{2+}]_i = 25 \times 0.01 / 100 = 2.5 \times 10^{-3}$
- $[CO_3^{2-}]_i = 75 \times 0.02 / 100 = 0.015$
- $Q_{ion} = (2.5 \times 10^{-3})(0.015) = 3.75 \times 10^{-5}$
- $Q > K$  ppt forms
- To determine the quantity of ppt, begin by assuming complete pptn limited by the limiting ion, in this case the  $Zn^{2+}$ . After this step  $[Zn^{2+}] = 0.00$  and  $[CO_3^{2-}] = 0.015 - 0.0025 = 0.0125$ .
- Next, check the amount of ppt that would “redissolve” to establish the saturated solution:  $2.5 \times 10^{-10} = [Zn^{2+}] \times 0.0125$ ;  $[Zn^{2+}] = 2 \times 10^{-8}$ . This is a negligible amount due to the very large excess of carbonate
- moles of ppt =  $0.015M \times 0.10L = 0.0015$  moles
- grams =  $0.0015 \times 125.4 = 0.19g$

- How much ppt would form if you combined 25mL of 0.0010M magnesium nitrate with 50mL of .0015M sodium fluoride?

# Separating two ions

If there is an anion which ppts both cations, it may still be used to separate them, if the resultant salts differ sufficiently in their solubilities. This is a more complex situation and requires detailed calculations.

- Assume you had a mixture of  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$ , both at 0.005M. Can they be separated using carbonate? Assume that the carbonate can be added very slowly at low concentration
- Step 1-at what carbonate concentration would each solid form-in this case, since the salts are 1:1, divide the  $K_{sp}$ s by 0.005, This yields threshold of carbonate of  $1.6 \times 10^{-6}$  for  $\text{Ba}^{2+}$  and  $2 \times 10^{-3}$  for the  $\text{Mg}^{2+}$ . Thus, the barium ion will ppt first
- One needs to have a standard for complete separation and this can be somewhat arbitrary, based upon the specific situation. For this problem, let's state that we need to remove 99.5% of the barium prior to the ppt of the  $\text{Mg}^{2+}$ . This requires that  $[\text{Ba}^{2+}] = 2.5 \times 10^{-5}$ . When  $[\text{Ba}^{2+}] = 2.5 \times 10^{-5}$ , the carbonate =  $1 \times 10^{-4}$ . This is below than the point at which magnesium begins to ppt, so separation is possible.

- A solution contains  $\text{Sn}^{2+}$  and  $\text{Cr}^{3+}$  at concentrations of 0.020M and 0.0010M concentrations, respectively.
  - Ksps:  $\text{Sn}(\text{OH})_2=5.4*10^{-27}$     $\text{Cr}(\text{OH})_3=6.7*10^{-31}$
- Analyze the potential of hydroxide ion to separate the two ions at the 99.5% level
- At what  $[\text{OH}^-]$  would each ion ppt?
  - Sn:  $[\text{OH}^-]=(5.4*10^{-27}/.020)^{1/2}=5.2*10^{-13}$
  - $\text{Cr}^{3+}$ :  $[\text{OH}^-]=(6.7*10^{-31}/.001)^{1/3}=8.7*10^{-10}$
  - $\text{Sn}^{2+}$  ppts first
- 99.5% removal of  $\text{Sn}^{2+}$  would result in the  $[\text{Sn}^{2+}]=1*10^{-4}$
- when  $[\text{Sn}^{2+}]=1*10^{-4}$  then  $[\text{OH}^-]=(6.7*10^{-31}/1*10^{-4})^{1/2}=8.2*10^{-14}$ . This is below the point at which the  $\text{Cr}^{3+}$  will begin to ppt so separation at the 99.5% level is possible.



- Can sulfate ion be used to separate  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  from a solution where both cations are initially 0.010M? If not, what level of separation is possible for each ion?

# Entropy and Free Energy

- Regardless of how one wishes to actually describe it, entropy is the missing thermodynamic term that indicates whether or not a process is spontaneous.
- We will not be doing computations such as determining entropies of reactions by the combining the entropies of products and reagents (see section 17.4). but you should certainly be comfortable with the principles shown in equation 2 on p 765. The enthalpy and entropy of a process are combined in a term called the free energy,  $\Delta G$ .
- $\Delta G = \Delta H - T \Delta S$
- For a process to be spontaneous  $\Delta G < 0$ . Keep in mind the difference between  $\Delta G^\circ$  and  $\Delta G$
- Table 17.3 (p.737) summarizes the various combinations of  $\Delta H$  and  $\Delta S$  and the conditions under which each leads to spontaneity.
- A system at equilibrium has  $\Delta G = 0$
- Free energies behave just like enthalpies with regards to algebraic manipulation

# Summarizing Entropy

- Entropy is time's arrow-the entropy of the universe is increasing
- $\Delta S > 0$  favorable  $\Delta S < 0$  unfavorable  $\Delta S = q_{\text{rev}}/T$   $\Delta S = \Delta H/T$ . We will be limiting our calculations in this area to entropies of phase changes.  $S(\Delta S)$  has units J/K-mol or J/K. These are often called entropy units
- Spontaneity requires a total entropy change, system and universe, which is positive. Thus, for changes with  $\Delta S < 0$ ,  $\Delta H$  must be  $< 0$
- Predicting the sign of the entropy is usually possible, given sufficient detail about the starting and ending states. Predicting magnitudes is far more difficult
- The combination of entropy and enthalpy is the free energy,  $\Delta G$ .  $\Delta G = \Delta H - T\Delta S$ . Spontaneity requires  $\Delta G < 0$ . Equilibrium:  $\Delta G = 0$
- Four possible sets:  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ .
  - $\Delta H^\circ > 0$   $\Delta S^\circ > 0$  spontaneous above a minimum T
  - $\Delta H^\circ > 0$   $\Delta S^\circ < 0$  never spontaneous
  - $\Delta H^\circ < 0$   $\Delta S^\circ > 0$  always spontaneous
  - $\Delta H^\circ < 0$   $\Delta S^\circ < 0$  spontaneous below a maximum T
- Be aware that spontaneous and nonspontaneous is measured against the Q=1 condition. When the conditions are other than that, the direction of spontaneity can be different. Further,  $\Delta G$  represents the thermodynamic stability. The overall stability of a state requires consideration of its kinetic properties, as well.
- $\Delta G_{\text{rxn}} = \sum n^* \Delta G_{\text{prods}} - \sum n^* \Delta G_{\text{reacts}}$  you need to be able to use this equation
- $\Delta G^\circ = -RT \ln K$   $K = e^{-\Delta G^\circ/RT}$  Note that negative values of  $\Delta G^\circ$  lead to  $K > 1$ . You need to be able to use these two equations-the homework provides exercises .