General Chemistry II
PLI Sheet 13 AK
July 28, 2021

1. A solution is 1 x $10^{u\,4}$ M in NaI, Na_2SO_4, and Na_3PO_4. What would the order of precipitation be as a source of Pb^{2+} is added gradually to the solution? The relevant K_{sp} values are: K_{sp} PbI_2 = 8.5 x 10^{-9}; K_{sp} $PbSO_4$ = 1.8 x 10^{-8}; K_{sp} $Pb_3(PO_4)_2$ = 7.9 x 10^{-43}. (Hint: there is no need to use ICE charts here – try to determine where the K_{sp} is exceeded)

You cannot directly just compare K_{sp} values because the cation to anion ratio is not the same!! Setup three different reactions and evaluate each one independently to find the equilibrium Pb^{2+} in each case.

$$PbI_2(s) \leftrightarrow Pb^{2+}(aq) + 2I^-(aq)$$

$$K_{sp} = 8.5 * 10^{-9} = [Pb^{2+}][I^-]^2 = [Pb^{2+}](1 * 10^{-4}\,M)^2$$

$$[Pb^{2+}] = 0.85\,M$$

Consider the next solution.

$$PbSO_4(s) \leftrightarrow Pb^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = 1.8 * 10^{-8} = [Pb^{2+}][SO_4^{2-}] = [Pb^{2+}](1 * 10^{-4}\,M)$$

$$[Pb^{2+}] = 1.8 * 10^{-4}\,M$$

And finally, the last solution.

$$Pb_3(PO_4)_2(s) \leftrightarrow 3Pb^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$K_{sp} = 7.9 * 10^{-43} = [Pb^{2+}]^3[PO_4^{3-}]^2 = [Pb^{2+}]^3(1 * 10^{-4}\,M)^2$$

$$[Pb^{2+}] = 4.29 * 10^{-12}\,M$$

To determine the order of precipitation, the one that has the lowest equilibrium Pb^{2+} concentration is the one that will precipitate first since Pb^{2+} is being added gradually. Thus, the order of precipitation is:

#1 $Pb_3(PO_4)_2$
#2 $PbSO_4$
#3 PbI_2

2. **Fill in the blanks in the following table. Both ΔH and ΔS refer to the system.**

ΔH	ΔS	ΔG	Low Temp	High temp
-	+	-	Spontaneous	Spontaneous
-	-	Temp. dependent	Spontaneous	Non-spontaneous
+	+	Temp. dependent	Non-spontaneous	Spontaneous
+	-	+	Non-spontaneous	Non-spontaneous

3. Calculate ΔH°, ΔS°, and ΔG° for the following reaction to determine if it is spontaneous at 25°C.

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

Compound	ΔH_f° (kJ/mol)	ΔS° (J/K*mol)
NH_4NO_3 (s)	-365.56	151.08
NH_4^+ (aq)	-132.51	113.4
NO_3^- (aq)	-205.0	146.4

$$\Delta H^\circ = \Delta H_f^\circ{}_{products} - \Delta H_f^\circ{}_{reactants}$$

$$= \left[\left(1\ mol\ NH_4^+ * -132.51\frac{kJ}{mol}\right) + \left(1\ mol\ NO_3^- * -205.0\frac{kJ}{mol}\right)\right]$$

$$- \left[1\ mol\ NH_4NO_3 * -365.56\frac{kJ}{mol}\right] = 28.05\ kJ$$

$$\Delta S° = \Delta S°_{products} - \Delta S°_{reactants}$$
$$= \left[\left(1\ mol\ NH_4^+ * 113.4\frac{J}{mol * K}\right) + \left(1\ mol\ NO_3^- * 146.4\frac{J}{mol * K}\right)\right]$$
$$- \left[1\ mol\ NH_4NO_3 * 151.08\frac{J}{mol * K}\right] = 108.72\frac{J}{K}$$

$$\Delta G° = \Delta H° - T\Delta S° = 28.05\ kJ - (298.15\ K)\left(0.10872\frac{kJ}{K}\right) = -4.36\ kJ$$

Since ΔG° is negative, the reaction is spontaneous.

4. An unknown metal M forms an ionic hydroxide with the formula $M(OH)_2$ that exhibits the equilibrium…

$$M(OH)_2\ (s) \leftrightarrow M^{2+}\ (aq) + 2OH^-(aq)$$

…in a saturated aqueous solution. If the solution pH is 10, what is the solubility product constant K_{sp} of the compound?

The $K_{sp} = [M^{2+}][OH^-]^2$

If pH is 10, it means pOH is 4 and $[OH^-]$ is 10^{-4}. According to stoichiometry, the $[M^{2+}]$ must be 5^{-5}. Plugging this into the equation yields $K_{sp} = [5^{-5}][10^{-4}]^2$ $=5 \times 10^{-13}$

5. If the solubility product constant K_{sp} for $NaC_9H_7O_4$ is estimated to be 34.9, what is the approximate acetylsalicylate ion concentration in a saturated $NaC_9H_7O_4$ solution used for the reaction?

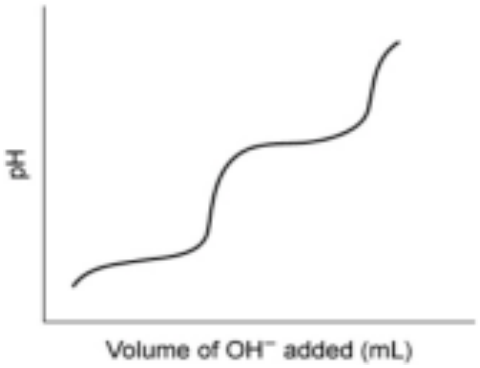
5.91 M

$K_{sp} = [Na^+][C_9H_7O_4^-]$

Since the sodium and acetylsalicylate ions form the compound of interest in a 1:1 ratio, $K_{sp} = x^2$ $x = 5.91$ M

MCAT Style Questions

6. The figure below shows the titration curve for an acid titrated with aqueous sodium hydroxide. When titrated in solution, which of the following salts would be most likely to produce a similar titration curve?



a. $(NH_4)_3PO_4$
b. KH_2PO_4
c. Na_2HPO_4
d. K_3PO_4

7. Suppose that citric acid ($H_3C_6H_5O_7$) is titrated with 0.1 M NaOH to form a citrate buffer solution with a pH of 4.5. What is the pH at the first equivalence point? (Note: pK_a1 = 3.13, pK_a2 = 4.76, pK_a3 = 6.40)

a. Less than 3.13
b. Between 3.13 and 4.76
c. Equal to 3.13
d. Greater than 4.76

8. Which of the following compound pairs, dissolved into solution at equal concentrations, will function as a buffer?

a. CH_3COOH (aq) and CH_3COONa (aq)
b. HNO_3 (aq) and $NaNO_3$ (aq)
c. NaBr (aq) and NaCN (aq)
d. NaOH (aq) and NaCl (aq)

9 . Consider a solution of magnesium hydroxide, $K_{sp} = 8.9 \times 10^{-12}$. solid magnesium hydroxide begins to precipitate when which of the following expressions is true? a. $[OH^-] < 1 \times 10^{-7}$
b. $[Mg^{2+}] = 8.9 \times 10^{-12}$
c. $[OH^-] = [Mg^{2+}]$
d. $[Mg^{2+}][OH^-]^2 > 8.9 \times 10^{-12}$

10. Suppose that a research technician wants to separate an aqueous mixture of CuF_2 and BaF_2 ($K_{sp} = 3.0 \times 10^{-6}$) by precipitating CuF_2 from the solution. What should be added to the solution to perform the separation?

a. $Cu(NO_3)_2$

b. NaF
c. $Ba(NO_3)_2$
d. H_2O