Solutions - Chapter 6

15. $Ag_4Fe(CN)_6(s) = 4Ag^{+} + Fe(CN)_6^{4-}$

1.0^{-6} x where x is the solubility in mol/L.

$$K_{sp} := 8.5\cdot10^{-45}$$

$$\left(10^{-6}\right)^4\cdot x = K_{sp} \qquad x := 10^{24}\cdot\left(8.5\cdot10^{-45}\right)$$

$x = 8.5 \text{ x } 10^{-21} = 8.5$ zM

16. $Cu(OH)_{1.5}(SO_4)_{0.25}(s) = Cu^{+2} + 3/2\ OH^{-} + 1/4\ SO_4^{2-}$ A Different look!

x $1.0x10^{-6}$ x/4 where x = solubility in mol/L

Equilibrium constant: $K = C_{Cu}\cdot C_{OH}^{\frac{3}{2}}\cdot C_{SO4}^{\frac{1}{4}}$ $\qquad K := 6.9\cdot10^{-18}$

Substituting for concentrations and K in the above expression;

$$x\cdot\left(1.0\cdot10^{-6}\right)^{\frac{3}{2}}\cdot\left(\frac{x}{4}\right)^{\frac{1}{4}} = 6.9\cdot10^{-18}$$ simplifies to $$7.071\times10^{-10}\cdot x^{\left(\frac{5}{4}\right)} = 6.9\cdot10^{-18}$$

$$x := 3.90\cdot10^{-7}$$

17. (a) $Zn_2Fe(CN)_6(s) = 2Zn^{+2} + Fe(CN)_6^{-4}$

$0.10x10^{-3}$ x where x is the solubility of $Zn_2Fe(CN)_6$ in mol/L.

No other ions present and ionic conc. from the solubility is negligible.

$$K_{sp} := 2.1\cdot10^{-16}$$

For solubility eqlm.; $\left(0.10\cdot10^{-3}\right)^2\cdot x = 2.1\cdot10^{-16}$

$$x := 2.10\cdot10^{-8}$$

(b) $Zn_2Fe(CN)_6(s) = 2Zn^{+2} + Fe(CN)_6^{4-}$

$5.0*10^{-7}$ x where x is the solubility in mol/L

The equilibrium expression is;

$$\left(5.0\cdot 10^{-7}\right)^2\cdot x = 2.1\cdot 10^{-16}$$

$$x := 8.40\cdot 10^{-4}$$

19. $K_{spCaSO4} := 2.4\cdot 10^{-5}$ $K_{spAg2SO4} := 1.5\cdot 10^{-5}$

solubility of Ca salt is lower than that of silver salt. Make sure you know why it is not always obvious. Original C_{Ca} = 0.0500, C_{Ag} = 0.0300.

Thus removing Ca ions as sulfate by 99% without precipitating silver is the task at hand. If 99% of Ca ions are precipitated (1% remain in solution) with no silver precipitating the conc. of the ions in solution are;

$C_{Ca} := .01\cdot 0.0500$ $C_{Ag} := 0.0300$

At that point the *conc of sulfate* in solution is given by the Ksp expression;

$$C_{Ca}\cdot C_{sulfate} = K_{spCaSO4}$$

has solution(s)

$$C_{sulfate} := \frac{K_{spCaSO4}}{C_{Ca}} \qquad C_{sulfate} = 0.048$$

Now, for silver sulfate solubility; Ag_2SO_4 = 2 Ag^+ + SO_4^{-2} ; $Q := C_{Ag}^{\ 2}\cdot C_{sulfate}$

If Q > $K_{spAg2SO4}$ (= $1.5\cdot 10^{-5}$) the the reverse reaction occurs, i.e. silver sulfate precipitates.

$Q = 4.32\times 10^{-5}$ i.e.. silver sulfate would precipitate when 99% of calcium is pptd.

Answer; NO, silver ions would precipitate if 99% Ca is precicipitated.

At the point where silver sulfate is just at the brink of precipitation, the sulfate ion conc. in solution will be given by;

$$K_{spAg2SO4} = C_{Ag}^{\ 2}\cdot C_{sulfate}$$

has solution(s)

$$C_{sulfate} := \frac{K_{spAg2SO4}}{C_{Ag}^{\ 2}} \qquad C_{sulfate} = 0.017$$

Just at the brink of silver precipitation the calcium ion concentration in solution is;

$$K_{spCaSO4} = C_{Ca} \cdot C_{sulfate}$$

has solution(s)

$$C_{Ca} := \frac{K_{spCaSO4}}{C_{sulfate}} \qquad C_{Ca} = 1.44 \times 10^{-3}$$

The percentage of Ca ions precipitated at that point is;

$$\frac{0.050 - 1.44 \times 10^{-3}}{0.050} \cdot 100 = 97.12$$

23. Lewis acids: BF_3, AsF_5

25. For the set of equilibria,
Given Data are;

$$K_{sp} := 3.0 \cdot 10^{-16} \qquad \beta_1 := 1 \cdot 10^{4} \qquad \beta_2 := 2 \cdot 10^{10}$$

$$\beta_3 := 8 \cdot 10^{13} \qquad \beta_4 := 3 \cdot 10^{15}$$

$$C_{OH} := 3.2 \cdot 10^{-7}$$

Initial Guesses:

$$C_{Zn} := 10^{-8} \qquad C_{ZnOH} := 10^{-8} \qquad C_{ZnO2H2} := 10^{-8} \qquad C_{ZnO3H3} := 10^{-8} \qquad C_{ZnO4H4} := 10^{-8}$$

Given

$$C_{Zn} = \frac{K_{sp}}{C_{OH}^{2}}$$

rearranged equations.

$$C_{ZnOH} = \beta_1 \cdot C_{Zn} \cdot C_{OH}$$

$$C_{ZnO2H2} = \beta_2 \cdot C_{Zn} \cdot C_{OH}^{2}$$

$$C_{ZnO3H3} = \beta_3 \cdot C_{Zn} \cdot C_{OH}^{3}$$

$$C_{ZnO4H4} = \beta_4 \cdot C_{Zn} \cdot C_{OH}^{4}$$

notice the four independent equations.
solution of this problem greately simplified by the recogninition that C_{OH} is fixed.

$$\begin{pmatrix} C_{Zn} \\ C_{ZnOH} \\ C_{ZnO2H2} \\ C_{ZnO3H3} \\ C_{ZnO4H4} \end{pmatrix} := \mathrm{Find}(C_{Zn}, C_{ZnOH}, C_{ZnO2H2}, C_{ZnO3H3}, C_{ZnO4H4})$$

Solves as;

$$\begin{pmatrix} C_{Zn} \\ C_{ZnOH} \\ C_{ZnO2H2} \\ C_{ZnO3H3} \\ C_{ZnO4H4} \end{pmatrix} = \begin{pmatrix} 2.93 \times 10^{-3} \\ 9.375 \times 10^{-6} \\ 6 \times 10^{-6} \\ 7.68 \times 10^{-9} \\ 9.216 \times 10^{-14} \end{pmatrix}$$

35.	acid	base
(a)	H_3O^+	H_2O (extra example)
(b)	$H_3N^+CH_2CH_2NH_3^+$	$H_3N^+CH_2CH_2NH_2$
(c)	$C_6H_5CO_2H$	$C_6H_5CO_2^-$
(d)	$C_5H_5NH^+$	C_5H_5N (extra example)

39. From tables; $K_{sp} := 2 \cdot 10^{-21}$

$C_{La} := 0.010$ $\quad K_w := 1.0 \cdot 10^{-14}$

By definition; $C_{La} \cdot C_{OH}^{\ 3} = K_{sp}$

Solving for C_{OH};

$$C_{OH} := \left(\frac{K_{sp}}{C_{La}}\right)^{\frac{1}{3}}$$

In aqueous system $pH := -\log\left(\frac{K_w}{C_{OH}}\right)$ $pH = 7.767$

45. $C_5H_5N + H_2O = C_5H_5NH^+ + OH^-$

$HOCH_2CH_2S^- + H_2O = HOCH_2CH_2SH + OH^-$

54 Regardless of the planet this problem considers the $CaCO_3(s)$ solubility in water.

The dissolved carbonate ions establishes a series of equilibria, which involves the CO_2 in the atmosphere.

(1) $CO_2(g) = CO_2\ (aq)$ K_{CO2}

(2) $CO_2(aq) + H_2O(l) = HCO_3^-(aq) + H^+(aq)$ K_1

(3) $HCO_3^-(aq) = CO_3^{-2}(aq) + H^+(aq)$ K_2

(4) $CO_3^-(aq) + Ca^{+2}(aq) = CaCO_3(s)$ $1/K_{sp}$

addition of the above equilibria as written yields:

$CO_2(g) + H_2O\ (l) + Ca^{+2}(aq) = CaCO_3(s) + 2\ H^+(aq)$ associated with an equilibrium constant K as defined below.

$K_{sp} := 6.0\cdot 10^{-9}$ $K_{CO2} := 3.4\cdot 10^{-2}$ $K_1 := 4.4\cdot 10^{-7}$ $K_2 := 4.7\cdot 10^{-11}$

$P_{CO2} := 0.10$ $C_H := 1.8\cdot 10^{-7}$

$$K := K_{CO2}\cdot K_1\cdot K_2\cdot\frac{1}{K_{sp}}$$

K expressed as $\frac{C_H{}^2}{P_{CO2}\cdot C_{Ca}} = K_{CO2}\cdot K_1\cdot K_2\cdot\frac{1}{K_{sp}}$ has solution(s)

$$C_{Ca} := C_H{}^2\cdot\frac{K_{sp}}{\left[K_{CO2}\cdot\left[K_1\cdot\left(K_2\cdot P_{CO2}\right)\right]\right]}$$ $C_{Ca} = 2.765\times 10^{-3}$

In 2 liters mass of Ca(II) in grams; $C_{Ca}\cdot 40.078\cdot 2 = 0.222$