

Homework 16–6: Problems pg. 724 #64, 65, 67, 68, 72, 74, 76

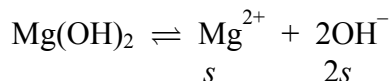
64 Which of the following will be more soluble in acid solution than in pure water?

- (a) **CuI:** no, since I^- (aq) does not hydrolyze
- (b) **Ag_2SO_4 :** yes, since SO_4^{2-} (aq) is a weak base (conj. base of HSO_4^-)
- (c) **$\text{Zn}(\text{OH})_2$:** yes, since OH^- (aq) is a strong base (conj. base of H_2O)
- (d) **BaC_2O_4 :** yes, since $\text{C}_2\text{O}_4^{2-}$ (aq) is a weak base (conj. base of HC_2O_4^-)
- (e) **$\text{Ca}_3(\text{PO}_4)_2$:** yes, since PO_4^{3-} (aq) is a weak base (conj. base of HPO_4^{2-})

The solubilities (b) through (e) will increase in acidic solution. Only (a), which contains an extremely weak base (I^- is the conjugate base of the strong acid HI) is unaffected by the acid solution.

65 Compare the molar solubility of $\text{Mg}(\text{OH})_2$ in water and in a solution buffered at a pH of 9.0.

In water:



$$K_{\text{sp}} = 4s^3 = 1.2 \times 10^{-11}; s = 1.4 \times 10^{-4} \text{ M}$$

In a buffer at pH = 9.0

$$[\text{H}^+] = 1.0 \times 10^{-9}; [\text{OH}^-] = 1.0 \times 10^{-5}$$

$$1.2 \times 10^{-11} = (s)(1.0 \times 10^{-5})^2; s = 0.12 \text{ M}$$

It seems counter-intuitive that the $\text{Mg}(\text{OH})_2$ should have a HIGHER solubility at a HIGHER $[\text{OH}^-]_0$. However, remember that in the first case, the dissolution of $\text{Mg}(\text{OH})_2$ is putting $1.4 \times 10^{-4} \text{ M OH}^-$ into solution to add to the $1.0 \times 10^{-7} \text{ M}$ from H_2O , so pH is not constant. In the second case, the buffer is removing the OH^- from solution as it is produced so the solubility equilibrium is pulled to the right. If the first situation were buffered at pH = 7, it *would* have a higher solubility.

67 The solubility product of $\text{Mg}(\text{OH})_2$ is 1.2×10^{-11} . What minimum OH^- concentration must be attained (for example, by adding NaOH) to decrease the Mg^{2+} concentration in a solution of $\text{Mg}(\text{NO}_3)_2$ to less than $1.0 \times 10^{-10} \text{ M}$?

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$$

$$\text{When } [\text{Mg}^{2+}] \text{ is } 1.0 \times 10^{-10} \text{ M, } [\text{OH}^-] = \left(\frac{1.2 \times 10^{-11}}{1.0 \times 10^{-10}} \right)^{\frac{1}{2}} = 0.35 \text{ M}$$

Therefore $[\text{OH}^-]$ must be $\geq 0.35 \text{ M}$.

68 Calculate whether or not a precipitate will form if 2.00 mL of 0.60 M NH_3 are added to 1.0 L of $1.0 \times 10^{-3} \text{ M FeSO}_4$.

We first determine the effect of the added ammonia. Let's calculate the concentration of NH_3 . This is a dilution problem.

$$\begin{aligned} M_i V_i &= M_f V_f \\ (0.60 \text{ M})(2.00 \text{ mL}) &= M_f (1002 \text{ mL}) \\ M_f &= 0.0012 \text{ M NH}_3 \end{aligned}$$

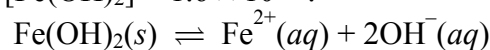
Ammonia is a weak base ($K_b = 1.8 \times 10^{-5}$) that produces OH^- :

	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	
Initial (M):	0.0012	0 0
Change (M):	-x	+x +x
Equil. (M):	0.0012 - x	x x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}; 1.8 \times 10^{-5} = \frac{x^2}{(0.0012 - x)}$$

Solving the resulting quadratic equation gives $x = 0.00014$, or $[\text{OH}^-] = 0.00014 \text{ M}$

This solution of iron(II) sulfate contains Fe^{2+} , which could combine with OH^- to precipitate $\text{Fe}(\text{OH})_2$. $K_{\text{sp}} [\text{Fe}(\text{OH})_2] = 1.6 \times 10^{-14}$:



$$Q = [\text{Fe}^{2+}]_0[\text{OH}^-]_0^2 = (1.0 \times 10^{-3})(0.00014)^2 = 2.0 \times 10^{-11}$$

Q is larger than K_{sp} ; therefore, a precipitate of $\text{Fe}(\text{OH})_2$ will form.

72 Calculate the concentrations of Cd^{2+} , $\text{Cd}(\text{CN})_4^{2-}$, and CN^- at equilibrium when 0.50 g of $\text{Cd}(\text{NO}_3)_2$ dissolves in $5.0 \times 10^2 \text{ mL}$ of 0.50 M NaCN.

First calculate the initial concentration of Cd^{2+} ions.

$$[\text{Cd}^{2+}]_0 = \frac{0.50 \text{ g} \times \frac{1 \text{ mol Cd}(\text{NO}_3)_2}{236.42 \text{ g Cd}(\text{NO}_3)_2} \times \frac{1 \text{ mol Cd}^{2+}}{1 \text{ mol Cd}(\text{NO}_3)_2}}{0.50 \text{ L}} = 4.2 \times 10^{-3} \text{ M}$$

First assume that the above equilibrium goes to completion (to avoid solving a 4th order polynomial):

	$\text{Cd}^{2+}(\text{aq}) + 4\text{CN}^-(\text{aq}) \longrightarrow \text{Cd}(\text{CN})_4^{2-}(\text{aq})$
Initial (M):	4.2×10^{-3} 0.50 0
Change (M):	-4.2×10^{-3} $-4(4.2 \times 10^{-3})$ $+4.2 \times 10^{-3}$
Final (M):	0 0.48 4.2×10^{-3}

To find the concentration of these species at equilibrium, re-equilibrate (since $[\text{Cd}^{2+}]$ can't be zero) using the formation constant expression:

	$\text{Cd}^{2+}(\text{aq}) + 4\text{CN}^-(\text{aq}) \rightleftharpoons \text{Cd}(\text{CN})_4^{2-}(\text{aq})$
Initial (M):	0 0.48 4.2×10^{-3}
Change (M):	+x +4x -x
Equilibrium (M):	x $0.48 + 4x$ $4.2 \times 10^{-3} - x$

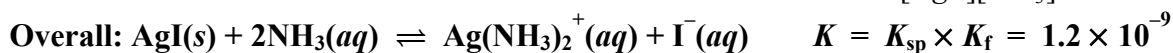
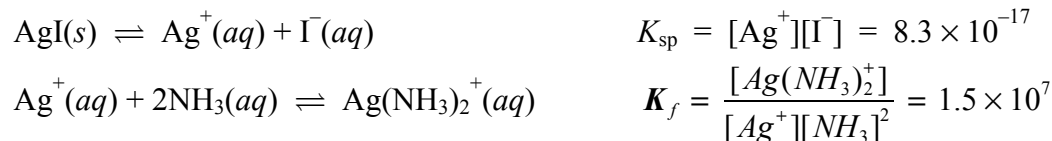
$$K_f = 7.1 \times 10^{16} = \frac{[4.2 \times 10^{-3} - x]}{[x][0.48 + 4x]^4} \approx \frac{[4.2 \times 10^{-3}]}{[x][0.48]^4}, \text{ or } [\text{Cd}^{2+}] = x = \frac{4.2 \times 10^{-3}}{(7.1 \times 10^{16})(0.48)^4} = 1.1 \times 10^{-18} \text{ M}$$

$$[\text{CN}^-] = 0.48 \text{ M} + 4(1.1 \times 10^{-18} \text{ M}) = 0.48 \text{ M}$$

$$[\text{Cd}(\text{CN})_4^{2-}] = (4.2 \times 10^{-3} \text{ M}) - (1.1 \times 10^{-18}) = 4.2 \times 10^{-3} \text{ M}$$

Check: Substitute the equilibrium concentrations calculated into the formation constant expression to calculate K_f . Also, the small value of $[\text{Cd}^{2+}]$ at equilibrium, compared to its initial concentration of $4.2 \times 10^{-3} M$, certainly justifies our approximation that almost all the Cd^{2+} ions react.

74 Calculate the molar solubility of AgI in a $1.0 M \text{NH}_3$ solution.



	$\text{AgI}(s)$	$+ 2\text{NH}_3(aq)$	\rightleftharpoons	$\text{Ag}(\text{NH}_3)_2^+(aq)$	$+ \text{I}^-(aq)$
Initial (M):		1.0		0.0	0.0
Change (M):	-s	-2s		+s	+s
Equilibrium (M):	(1.0 - 2s)	s		s	s

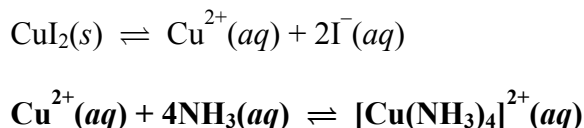
We can write the equilibrium constant expression for the above reaction, then solve for s .

$$\begin{aligned} K &= 1.2 \times 10^{-9} = \frac{(s)(s)}{(1.0 - 2s)^2} \approx \frac{(s)(s)}{(1.0)^2} \\ s &= 3.5 \times 10^{-5} M \end{aligned}$$

76 Explain, with balanced ionic equations, why the following reactions occur:

(a) CuI_2 dissolves in ammonia solution.

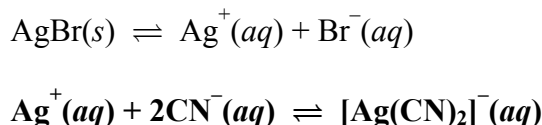
The equations are as follows:



The ammonia combines with the Cu^{2+} ions formed in the first step to form the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$, effectively removing the Cu^{2+} ions, causing the first equilibrium to shift to the right (resulting in more CuI_2 dissolving).

(b) AgBr dissolves in NaCN solution.

Similar to part (a):



(c) HgCl_2 dissolves in KCl solution.

Similar to parts (a) and (b).

