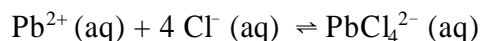


- The equation for the solubility equilibrium is: $\text{Ni}(\text{OH})_2 (\text{s}) \rightleftharpoons \text{Ni}^{2+} (\text{aq}) + 2 \text{OH}^- (\text{aq})$, so if x moles of $\text{Ni}(\text{OH})_2$ dissolve per liter of solution, $[\text{Ni}^{2+}] = x \text{ M}$ and $[\text{OH}^-] = 2x \text{ M}$,
 $K_{\text{sp}} = [\text{Ni}^{2+}] [\text{OH}^-]^2 = x (2x)^2 = 4x^3$.
- This is an example of the common ion effect. For CaSO_4 , $K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$. If the concentration of SO_4^{2-} is increased (relative to pure water) due to the presence of another source of SO_4^{2-} , $[\text{Ca}^{2+}]$ will necessarily be smaller (relative to pure water), resulting in a smaller solubility for CaSO_4 .
- For AgCl , $K_{\text{sp}} = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$.

$$\text{If } [\text{Cl}^-] = 0.10 \text{ M, } [\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{0.10} = 1.8 \times 10^{-9} \text{ M}$$

- We would have to know the concentrations of the ions, $[\text{Pb}^{2+}]$ and $[\text{I}^-]$ in the mixture, and we would have to know K_{sp} for PbI_2 . We can calculate $Q = [\text{Pb}^{2+}] [\text{I}^-]^2$ and compare Q to K_{sp} . If $Q > K_{\text{sp}}$, precipitation of PbI_2 will occur at equilibrium. If $Q < K_{\text{sp}}$, no precipitation would occur.
- HF is a weak acid, so F^- reacts with H_3O^+ to form HF . This reduces the F^- ion concentration, causing more BaF_2 to dissolve. In water, the H_3O^+ concentration is not sufficiently high to cause a significant amount of F^- to hydrolyze to HF .
- By carefully controlling pH, the S^{2-} concentration in a solution of H_2S can be adjusted so to a level allowing PbS to precipitate but not ZnS .
- When Cl^- is first added to a solution containing Pb^{2+} , PbCl_2 first precipitates. When the Cl^- concentration becomes sufficiently large, a second equilibrium comes into play:



This equilibrium reduces the Pb^{2+} concentration to a point where the PbCl_2 will dissolve.

- At first, $\text{Al}(\text{OH})_3$ precipitates from the solution. However, $\text{Al}(\text{OH})_3$ is an amphoteric hydroxide which will react with additional OH^- producing $\text{Al}(\text{OH})_4^-$, causing the $\text{Al}(\text{OH})_3$ to dissolve as the OH^- concentration is raised.
- AgCl is more soluble than AgI . (AgCl has the larger value of K_{sp} .)
 - $\text{Mg}(\text{OH})_2$ is more soluble than $\text{Cu}(\text{OH})_2$. ($\text{Mg}(\text{OH})_2$ has the larger value of K_{sp} .)

Note: To determine relative solubility by comparing K_{sp} , the stoichiometry of the two compounds must be the same.

13. Since the solution is already saturated with respect to PbCl_2 , any additional Cl^- added to the solution will cause the immediate precipitation of additional PbCl_2 . We could say the same thing for the Pb^{2+} ions from a saturated solution of PbS , however, their concentration is extremely small ($\sim 5 \times 10^{-14} M$) that the Cl^- ions from $0.1 M \text{NaCl}$ would produce more precipitate for a given volume. The $0.1 M \text{Na}_2\text{SO}_4$ solution would not cause a precipitate to form until enough is added to make $[\text{SO}_4^{2-}] = 1.1 \times 10^{-6} M$.
17. We would add sufficient SO_4^{2-} to precipitate essentially all of the Ba^{2+} , but none of the Ca^{2+} . The solid BaSO_4 could then be removed by filtration. Additional SO_4^{2-} could then be added to the remaining solution to precipitate the Ca^{2+} . The solid CaSO_4 can then be removed by filtration, leaving behind a solution that contains Mg^{2+} .
19. a. NaBr and $(\text{NH}_4)_2\text{SO}_4$ are soluble. BaCO_3 and PbI_2 are insoluble.
21. a. $K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$
 b. $K_{\text{sp}} = [\text{Sr}^{2+}][\text{CO}_3^{2-}]$
 c. $K_{\text{sp}} = [\text{Ca}^{2+}]^3 [\text{AsO}_4^{3-}]^2$
 d. $K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3$

$$23. \quad \frac{0.0072 \text{ g}}{\text{L}} \times \frac{1 \text{ mol}}{235.77 \text{ g}} = 3.05 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

$$[\text{Ag}^+] = [\text{BrO}_3^-] = 3.05 \times 10^{-5} M \quad K_{\text{sp}} = [\text{Ag}^+][\text{BrO}_3^-] = (3.05 \times 10^{-5})^2 = 9.3 \times 10^{-10}$$

$$25. \quad \frac{0.13 \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol}}{413.35 \text{ g}} = 3.14 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$[\text{Cu}^{2+}] = 3.14 \times 10^{-3} M \quad [\text{IO}_3^-] = 6.28 \times 10^{-3} M$$

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (3.14 \times 10^{-3})(6.28 \times 10^{-3})^2 = 1.2 \times 10^{-7}$$

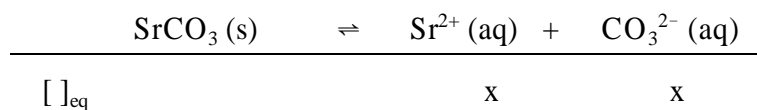
$$27. \quad \text{pH} = 10.52 \quad \text{pOH} = 14.00 - 10.52 = 3.48$$

$$[\text{OH}^-] = 10^{-3.48} = 3.31 \times 10^{-4} M$$

$$[\text{Mg}^{2+}] = \frac{1}{2} [\text{OH}^-] = 1.65 \times 10^{-4} M$$

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (1.65 \times 10^{-4})(3.31 \times 10^{-4})^2 = 1.8 \times 10^{-11}$$

29.

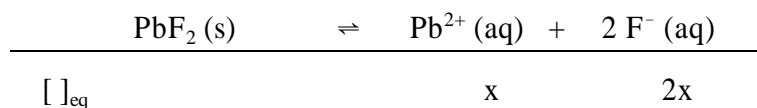


$$K_{\text{sp}} = 9.3 \times 10^{-10} = [\text{Sr}^{2+}][\text{CO}_3^{2-}] = x^2$$

$$x = \sqrt{9.3 \times 10^{-10}} = 3.04 \times 10^{-5} \text{ M}$$

$$\frac{3.04 \times 10^{-5} \text{ mol}}{\text{L}} \times \frac{147.63 \text{ g}}{1 \text{ mol}} = 4.5 \times 10^{-3} \frac{\text{g}}{\text{L}}$$

31.

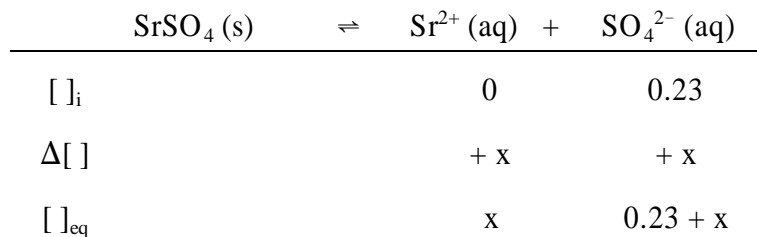


$$K_{\text{sp}} = 2.7 \times 10^{-8} = [\text{Pb}^{2+}][\text{F}^{-}]^2 = (x)(2x)^2 = 4x^3$$

$$x = \sqrt[3]{\frac{2.7 \times 10^{-8}}{4}} = 1.9 \times 10^{-3} \text{ M}$$

$$\frac{1.9 \times 10^{-3} \text{ mol}}{\text{L}} \times \frac{245.2 \text{ g}}{1 \text{ mol}} = 0.47 \frac{\text{g}}{\text{L}}$$

33.



$$K_{\text{sp}} = 2.5 \times 10^{-7} = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = (x)(0.23 + x)$$

Assume $x \ll 0.23$

$$2.5 \times 10^{-7} \approx (x)(0.23)$$

$$x = \frac{2.5 \times 10^{-7}}{0.23} = 1.08 \times 10^{-6} M \quad \frac{1.08 \times 10^{-6}}{0.23} \times 100 = 4.7 \times 10^{-4} \%$$

Assumption is justified: solubility = $[Sr^{2+}] = 1.08 \times 10^{-6} M$

$$\frac{1.08 \times 10^{-6} \text{ mol}}{L} \times \frac{183.68 \text{ g}}{1 \text{ mol}} = 2.0 \times 10^{-4} \frac{\text{g}}{L}$$

35. First, we use the solubility to calculate K_{sp} .

$$\frac{0.016 \text{ g}}{L} \times \frac{1 \text{ mol}}{62.30 \text{ g}} = 2.56 \times 10^{-4} M = [Mg^{2+}] \quad [F^-] = 5.12 \times 10^{-4} M$$

$$K_{sp} = [Mg^{2+}][F^-]^2 = (2.56 \times 10^{-4})(5.12 \times 10^{-4})^2 = 6.71 \times 10^{-11}$$

	MgF ₂ (s)	⇌	Mg ²⁺ (aq)	+	2 F ⁻ (aq)
[] _i			0		0.020
Δ[]			+ x		+ 2x
[] _{eq}			x		0.020 + 2x

$$K_{sp} = 6.71 \times 10^{-11} = [Mg^{2+}][F^-]^2 = (x)(0.015 + 2x)^2$$

Assume $2x \ll 0.020$

$$6.71 \times 10^{-11} \approx (x)(0.020)^2$$

$$x = \frac{6.71 \times 10^{-11}}{(0.020)^2} = 1.67 \times 10^{-7} M \quad \frac{2(1.67 \times 10^{-7})}{0.020} \times 100 = 1.7 \times 10^{-3} \%$$

Assumption is justified: solubility = $[Mg^{2+}] = 1.67 \times 10^{-7} M$

$$\frac{1.67 \times 10^{-7} \text{ mol}}{L} \times \frac{62.30 \text{ g}}{1 \text{ mol}} = 1.0 \times 10^{-5} \frac{\text{g}}{L}$$

37.

	$\text{MgC}_2\text{O}_4(\text{s})$	\rightleftharpoons	$\text{Mg}^{2+}(\text{aq})$	+	$\text{C}_2\text{O}_4^{2-}(\text{aq})$
$[\]_i$			0		0.020
$\Delta[\]$			+ x		+ x
$[\]_{\text{eq}}$			x		0.020 + x

$$K_{\text{sp}} = 8.5 \times 10^{-5} = [\text{Mg}^{2+}][\text{C}_2\text{O}_4^{2-}] = (x)(0.020 + x)$$

$$8.5 \times 10^{-5} = 0.020x + x^2$$

$$x^2 + 0.020x - 8.5 \times 10^{-5} = 0$$

Solving this quadratic equation: $x = -0.024$ or 0.0036 . We can immediately reject the negative root, so $x = 0.0036$

$$[\text{Mg}^{2+}] = 0.0036 \text{ M} = \text{molar solubility}$$

$$\frac{0.0036 \text{ mol}}{\text{L}} \times \frac{112.30 \text{ g}}{1 \text{ mol}} = 0.4 \frac{\text{g}}{\text{L}}$$

39. a. $Q = [\text{Ba}^{2+}][\text{F}^-]^2 = (0.020)(0.015)^2 = 4.5 \times 10^{-6}$ $K_{\text{sp}} = 1.0 \times 10^{-6}$

$Q > K_{\text{sp}}$, so a precipitate should form.

b. $Q = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (0.035)(0.15)^2 = 7.9 \times 10^{-4}$ $K_{\text{sp}} = 1.6 \times 10^{-5}$

$Q > K_{\text{sp}}$, so a precipitate should form.

41. $Q = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = (5.0 \times 10^{-4})(5.0 \times 10^{-5}) = 2.5 \times 10^{-8}$ $K_{\text{sp}} = 1.8 \times 10^{-14}$

$Q > K_{\text{sp}}$, so a precipitate should form.

43. If a precipitate forms, it will be $\text{Mg}(\text{OH})_2$. The concentrations we use in the expression for Q are half of those in the stock solutions since the mixing of equal volumes of the two solutions dilutes each ion by a factor of two.

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.0010)(0.000050)^2 = 2.5 \times 10^{-12}$$
 $K_{\text{sp}} = 1.8 \times 10^{-11}$

$Q < K_{\text{sp}}$, so a precipitate should not form.

45. If a precipitate forms, it will be BaF_2 . Concentrations following mixing are:

$$[\text{Ba}^{2+}] = 0.0015 \text{ M} \times \frac{45.0 \text{ mL}}{120.0 \text{ mL}} = 5.62 \times 10^{-4} \text{ M}$$

$$[\text{F}^-] = 0.0025 \text{ M} \times \frac{75.0 \text{ mL}}{120.0 \text{ mL}} = 1.56 \times 10^{-3} \text{ M}$$

$$Q = [\text{Ba}^{2+}][\text{F}^-]^2 = (5.62 \times 10^{-4})(1.56 \times 10^{-3})^2 = 1.36 \times 10^{-9} \quad K_{\text{sp}} = 1.0 \times 10^{-6}$$

$Q < K_{\text{sp}}$, so a precipitate should not form.

47. The concentration of Ca^{2+} required to precipitate CaSO_4 is:

$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}}}{[\text{SO}_4^{2-}]} = \frac{2.4 \times 10^{-5}}{0.020} = 1.2 \times 10^{-3} \text{ M}$$

$$\text{moles of Ca}^{2+} = 1.2 \times 10^{-3} \text{ M} \times 1.5 \text{ L} = 0.0018 \text{ mol Ca}^{2+} = 0.0018 \text{ mol CaCl}_2$$

49. (We will ignore the change in volume due to the addition of the AgNO_3 solution. This is reasonable since the solution is relatively concentrated.) To effect the precipitation of AgCl from a solution containing 0.015 M Cl^-

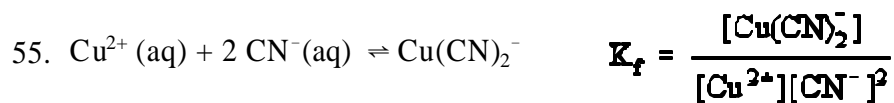
$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{0.015} = 1.2 \times 10^{-8} \text{ M}$$

When $[\text{Ag}^+] = 1.2 \times 10^{-8} \text{ M}$,

$$[\text{I}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{8.3 \times 10^{-17}}{1.2 \times 10^{-8}} = 6.9 \times 10^{-9} \text{ M}$$

51. $\text{BaF}_2(\text{s}) + 2 \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + 2 \text{HF}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$

53. HF is a weaker acid than HSO_4^- , so the BaF_2 should dissolve more readily.



57. This is a more complicated problem than it first appears. We will initially ignore the fact that AgCN is a sparingly soluble salt:

	Ag ⁺ (aq) +	2 CN ⁻ (aq)	⇌	Ag(CN) ₂ ⁻ (aq)
	0.015	0.100		0
	-0.015	-0.030		+0.015
[] _i	0	0.070		0.015
Δ[]	+x	+2x		-x
[] _{eq}	x	0.070 + 2x		0.015 - x

$$K_f = 5.6 \times 10^{18} = \frac{[\text{Ag}(\text{CN})_2^{-}]}{[\text{Ag}^{+}][\text{CN}^{-}]^2} = \frac{(0.015 - x)}{(x)(0.070 + 2x)^2}$$

Assume $x \ll 0.015$ and $2x \ll 0.070$

$$5.6 \times 10^{18} = \frac{(0.015)}{(x)(0.070)^2} = \frac{0.015}{(0.0049)x}$$

$$x = \frac{0.015}{(0.0049)(5.6 \times 10^{18})} = 5.5 \times 10^{-19} \text{ M} = [\text{Ag}^{+}] \quad (\text{Clearly negligible relative to } 0.015)$$

Check to see if AgCN will precipitate under these conditions:

$Q = (5.5 \times 10^{-19})(0.070) = 3.8 \times 10^{-20} < K_{sp} (2.2 \times 10^{-16})$, so AgCN will not precipitate.

59. This is also a much more complicated problem than it first appears, because $C_2O_4^{2-}$ is the anion of a weak acid. However, we will proceed by assuming the complex forms and calculating the concentration of free Cd^{2+} in equilibrium with the complex.

	$Cd^{2+} (aq) +$	$4 NH_3 (aq)$	\rightleftharpoons	$Cd(NH_3)_4^{2+} (aq)$
	0.0020	0.10		0
	-0.0020	- 0.0080		+ 0.0020
[] _i	0	0.092		0.0020
$\Delta[]$	+ x	+ 4x		- x
[] _{eq}	x	0.092 + 4x		0.0020 - x

$$K_f = 1.0 \times 10^7 = \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = \frac{(0.0020 - x)}{(x)(0.092 + 4x)^4}$$

Assume $x \ll 0.0020$ and $4x \ll 0.092$

$$1.0 \times 10^7 = \frac{(0.0020)}{(x)(0.092)^4}$$

$$x = \frac{0.0020}{(7.2 \times 10^{-5})(1.0 \times 10^7)} = 2.8 \times 10^{-6} M = [Cd^{2+}]$$

$$\frac{2.8 \times 10^{-6}}{0.0020} \times 100 = 0.14\%, \text{ so } x \text{ is much less than } 5\% \text{ of } 0.0020$$

Check to see if Cd^{2+} at this concentration will be precipitated by $0.010 M C_2O_4^{2-}$.

$$Q = [Cd^{2+}][C_2O_4^{2-}] = (2.8 \times 10^{-6})(0.010) = 2.8 \times 10^{-8} > K_{sp} (1.5 \times 10^{-8})$$

We would predict that CdC_2O_4 will precipitate.

$0.092 M NH_3$ has a pH of about 11.11. At this pH, α_2 for $H_2C_2O_4$ is ≈ 1 , so this calculation is reasonable. However, to be rigorous, we would need to consider all of these equilibria simultaneously. The calculation would involve at least 9 unknown concentrations!

61. Again, this is a much more complicated problem than it first appears, because $\text{C}_2\text{O}_4^{2-}$ is the anion of a weak acid. We will neglect its acid/base equilibrium as well as the ammonia acid/base equilibrium.

One mass balance equation is:

$$[\text{C}_2\text{O}_4^{2-}] = [\text{Cd}^{2+}] + [\text{Cd}(\text{NH}_3)_4^{2+}] \quad (\text{Neglecting partially formed complex})$$

A second mass balance equation is:

$$[\text{NH}_3] + 4 [\text{Cd}(\text{NH}_3)_4^{2+}] = 0.10$$

The equilibrium constant expression for the formation of the complex is a third equation:

$$K_f = \frac{[\text{Cd}(\text{NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = 1.0 \times 10^7$$

The solubility product expression is a fourth equation:

$$K_{sp} = 1.5 \times 10^{-8} = [\text{Cd}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

Solving this system of 4 equations gives:

$$[\text{C}_2\text{O}_4^{2-}] = 3.0 \times 10^{-2} \text{ M} = \text{solubility of CdC}_2\text{O}_4$$

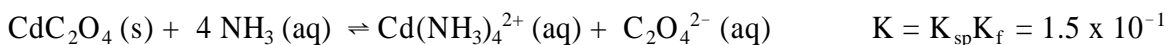
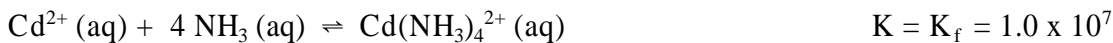
$$[\text{Cd}^{2+}] = 5.0 \times 10^{-2} \text{ M}$$

$$[\text{Cd}(\text{NH}_3)_4^{2+}] = 3.0 \times 10^{-2} \text{ M}$$

$$[\text{NH}_3] = 0.088 \text{ M}$$

We could approach this problem in another way:

If we combine the two equilibria



	$\text{CdC}_2\text{O}_4(\text{s}) + 4 \text{NH}_3(\text{aq})$	\rightleftharpoons	$\text{Cd}(\text{NH}_3)_4^{2+}(\text{aq}) +$	$\text{C}_2\text{O}_4^{2-}(\text{aq})$
$[\]_i$	0.10		0	0
$\Delta[\]$	- 4x		+x	+x
$[\]_{\text{eq}}$	$0.10 - 4x$		x	x

$$K_c = \frac{[\text{Cd}(\text{NH}_3)_4^{2+}][\text{C}_2\text{O}_4^{2-}]}{[\text{NH}_3]^4} = 1.5 \times 10^{-1}$$

$$K_c = \frac{(x)(x)}{(0.10 - 4x)^4} = 1.5 \times 10^{-1}$$

$$\frac{x}{(0.10 - 4x)^2} = \sqrt{1.5 \times 10^{-1}} = 0.387$$

$$6.2x^2 - 1.31x + 0.00387 = 0 \quad x = 0.21 \text{ or } 0.0030 \quad (\text{The first root is too large to be physically meaningful})$$

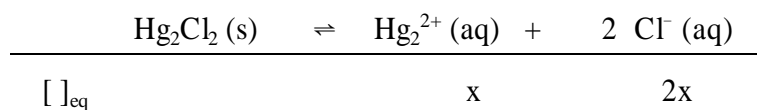
$$\text{Solubility} = [\text{C}_2\text{O}_4^{2-}] = 3.0 \times 10^{-2} M$$

63. Add HCl to precipitate the Pb^{2+} ion as PbCl_2 and filter the solid off. To the remaining solution, add dilute HCl and thioacetamide (a convenient source of H_2S in solution) to precipitate the Cd^{2+} ion as CdS . Sr^{2+} will remain in solution.
65. The fact that no precipitate formed when HCl was added indicates that Ag^+ is not in solution. (Ag^+ forms insoluble AgCl with Cl^- .) Since no precipitate formed on bubbling H_2S through the acidic solution, Cd^{2+} is not in the solution. (Cd^{2+} precipitates as CdS from acidic H_2S solutions.) Since a precipitate formed when the solution was made basic and had H_2S bubbled through it, the cation could be Mn^{2+} . If the compound contains only one cation, Ca^{2+} is not a possibility. However, if the compound contains two cations, Ca^{2+} is a possibility for one of them. None of the reactions described would precipitate Ca^{2+} ions.
67. Neglecting hydrolysis of SO_4^{2-} :

$$K_{\text{sp}} = 1.7 \times 10^{-8} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$\text{solubility} = [\text{Pb}^{2+}] = [\text{SO}_4^{2-}] = \sqrt{1.7 \times 10^{-8}} = 1.3 \times 10^{-4} M$$

69. a.

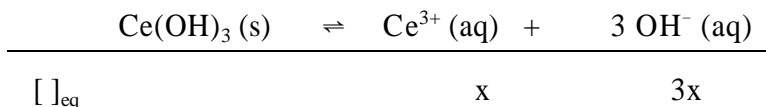


$$K_{\text{sp}} = 1.3 \times 10^{-18} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = 4x^3$$

$$\text{molar solubility} = x = \sqrt[3]{\frac{1.3 \times 10^{-18}}{4}} = 6.88 \times 10^{-7} \text{ M}$$

$$\text{b. solubility} = \frac{6.88 \times 10^{-7} \text{ mol}}{\text{L}} \times \frac{472.09 \text{ g}}{1 \text{ mol}} = 3.2 \times 10^{-4} \frac{\text{g}}{\text{L}}$$

71. a.



$$K_{\text{sp}} = 2.0 \times 10^{-20} = [\text{Ce}^{3+}][\text{OH}^-]^3 = 27x^4$$

$$\text{molar solubility} = x = \sqrt[4]{\frac{2.0 \times 10^{-20}}{27}} = 5.2 \times 10^{-6} \text{ M} = \frac{[\text{OH}^-]}{3}$$

$$\text{b. pOH} = -\log [\text{OH}^-] = -\log (1.56 \times 10^{-5}) = 4.81$$

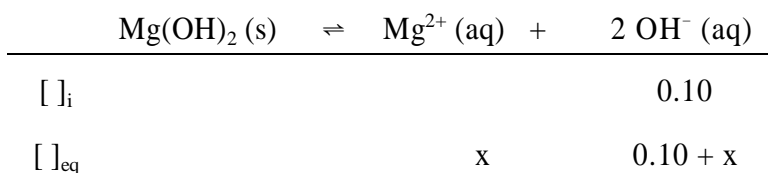
73. In a solution buffered at pH = 8.80, pOH = 5.20 and $[\text{OH}^-] = 10^{-5.20} = 6.3 \times 10^{-6} \text{ M}$.

$$K_{\text{sp}} = 1.8 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = [\text{Mg}^{2+}](6.3 \times 10^{-6})^2$$

$$\text{The molar solubility is given by } [\text{Mg}^{2+}] = \frac{1.8 \times 10^{-11}}{(6.3 \times 10^{-6})^2} = 0.452 \text{ M}$$

$$\text{solubility} = \frac{0.452 \text{ mol}}{\text{L}} \times \frac{58.31 \text{ g}}{1 \text{ mol}} = 26 \frac{\text{g}}{\text{L}}$$

75.



$$K_{\text{sp}} = 1.8 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (x)(0.10 + x)^2$$

Assume $x \ll 0.10$

$$1.8 \times 10^{-11} \approx (x)(0.10)^2 = 0.010 x$$

$$\text{molar solubility} = x = \frac{1.8 \times 10^{-11}}{0.010} = 1.8 \times 10^{-9} \text{ M}$$

77. To effect the precipitation of CaSO_4 , $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$ must just exceed K_{sp} .

$$\text{For } \text{CaSO}_4, K_{\text{sp}} = 2.4 \times 10^{-5} \quad [\text{Ca}^{2+}][\text{SO}_4^{2-}] > 2.4 \times 10^{-5} \quad \text{if } [\text{Ca}^{2+}] = 0.0030 \text{ M}$$

$$[\text{SO}_4^{2-}] > \frac{2.4 \times 10^{-5}}{0.0030} = 8.0 \times 10^{-9} \text{ M}$$

79. Concentrations following mixing are:

$$[\text{Pb}^{2+}] = 0.00125 \text{ M} \times \frac{3.20 \text{ L}}{4.00 \text{ L}} = 0.00100 \text{ M}$$

$$[\text{Cl}^-] = 0.50 \text{ M} \times \frac{0.80 \text{ L}}{4.20 \text{ L}} = 0.10 \text{ M}$$

$$Q = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (0.00100)(0.10)^2 = 1.0 \times 10^{-5} \quad K_{\text{sp}} = 1.6 \times 10^{-5}$$

$Q < K_{\text{sp}}$, so a the solution is unsaturated.

81. We will assume that no volume change occurs on the addition of solid NaCl to the solution.

To prevent a precipitate from forming, $[Ag^+][Cl^-] < K_{sp} = 1.8 \times 10^{-10}$

$$\text{If } [Ag^+] = 0.0015 \text{ M, then } [Cl^-] < \frac{1.8 \times 10^{-10}}{0.0015} = 1.2 \times 10^{-7} \text{ M}$$

$$1.2 \times 10^{-7} \text{ M} \times 0.785 \text{ L} = 9.42 \times 10^{-8} \text{ mol} \quad (\text{Less than } 9.42 \times 10^{-8} \text{ mol } Cl^- \text{ may be added})$$

$$9.42 \times 10^{-8} \text{ mol } Cl^- \times \frac{1 \text{ mol NaCl}}{1 \text{ mol } Cl^-} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol}} = 5.5 \times 10^{-6} \text{ g NaCl}$$

83. Since $K \gg 1$, assume the reaction goes to completion and approaches equilibrium from the products side.

	$Fe^{3+} (aq)$	+	$SCN^- (aq)$	\rightleftharpoons	$Fe(SCN)^{2+} (aq)$
	2.00		2.00		0
	-2.00		-2.00		+2.00
$[]_i$	0		0		2.00
$\Delta []$	+x		+x		-x
$[]_{eq}$	x		x		2.00 - x

$$K_f = 9.0 \times 10^2 = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(2.00 - x)}{(x)(x)}$$

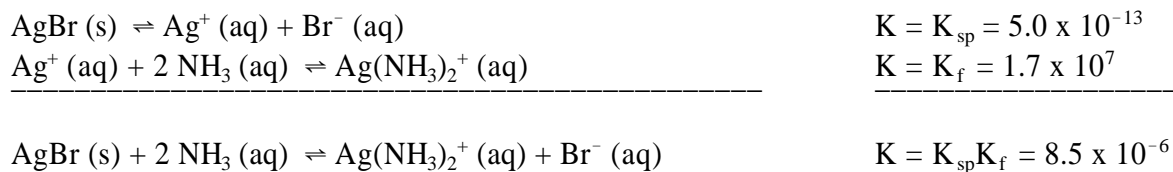
Assume $x \ll 2.00$

$$9.0 \times 10^2 = \frac{(2.00)}{(x)(x)}$$

$$x = \sqrt{\frac{2.00}{900}} = 4.7 \times 10^{-2} \quad \frac{4.7 \times 10^{-2}}{2.00} \times 100 = 2.35\% \quad \text{assumption is O.K.}$$

$$[Fe^{3+}] = x = 4.7 \times 10^{-2} \text{ M.}$$

85. We will take the approach we used in a previous problem where we combined the solubility and complex formation equilibria into a single equilibrium.



	AgBr (s) +	2 NH ₃ (aq)	⇌	Ag(NH ₃) ₂ ⁺ (aq) +	Br ⁻ (aq)
[] _i		5.0		0	0
Δ[]		- 2x		+x	+x
[] _{eq}		5.0 - 2x		x	x

$$K_{\text{c}} = \frac{[\text{Ag(NH}_3\text{)}_2^+][\text{Br}^-]}{[\text{NH}_3]^2} = 8.5 \times 10^{-6}$$

$$K_{\text{c}} = \frac{(x)(x)}{(5.0 - 2x)^2} = 8.5 \times 10^{-6}$$

Taking the square root of each side:

$$\frac{x}{(5.0 - 2x)} = \sqrt{8.5 \times 10^{-6}} = 2.9 \times 10^{-3}$$

$x = 0.014 \text{ M} =$ molar solubility of AgBr in 5.0 M NH_3 .

87. The oxalate ion concentration give the molar solubility of ZnC_2O_4 , so $[\text{C}_2\text{O}_4^{2-}] = 3.6 \times 10^{-4} \text{ M}$.

$$K_{\text{sp}} = 1.5 \times 10^{-9} = [\text{Zn}^{2+}][\text{C}_2\text{O}_4^{2-}] \quad [\text{Zn}^{2+}] = \frac{1.5 \times 10^{-9}}{3.6 \times 10^{-4}} = 4.16 \times 10^{-6} \text{ M}$$

$$[\text{C}_2\text{O}_4^{2-}] = [\text{Zn}^{2+}] + [\text{Zn(NH}_3\text{)}_4^{2+}]$$

$$\text{so } [\text{Zn(NH}_3\text{)}_4^{2+}] = [\text{C}_2\text{O}_4^{2-}] - [\text{Zn}^{2+}] = 3.6 \times 10^{-4} \text{ M} - 4.16 \times 10^{-6} \text{ M} = 3.56 \times 10^{-4} \text{ M}$$

At equilibrium, $[\text{NH}_3] = 0.0150 \text{ M} - 4(3.56 \times 10^{-4} \text{ M}) = 0.01357 \text{ M}$

$$K_{\text{f}} = \frac{[\text{Zn(NH}_3\text{)}_4^{2+}]}{[\text{Zn}^{2+}][\text{NH}_3]^4} = \frac{3.56 \times 10^{-4}}{(4.16 \times 10^{-6})(0.01357)^4} = 2.5 \times 10^9$$

89.

	NH ₃ (aq) +	H ₂ O (l)	⇌	NH ₄ ⁺ (aq) +	OH ⁻ (aq)
[] _i	0.10			0	~0
Δ[]	-x			+x	+x
[] _{eq}	0.10 - x			x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{0.10 - x}$$

Assume $x \ll 0.10$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.10}$$

$$x = \sqrt{(1.8 \times 10^{-5})(0.10)} = 1.3 \times 10^{-3} \quad \frac{1.3 \times 10^{-3}}{0.10} \times 100 = 1.3\% \quad \text{assumption O.K.}$$

$$[\text{OH}^-] = 1.3 \times 10^{-3} \text{ M}$$

For Mg(OH)₂ to precipitate, $[\text{Mg}^{2+}][\text{OH}^-]^2 > K_{sp} = 1.8 \times 10^{-11}$

$$[\text{Mg}^{2+}] > \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{1.8 \times 10^{-11}}{(1.3 \times 10^{-3})^2} = 1.1 \times 10^{-5} \text{ M}$$

91. K_{sp} is calculated from the solubility of Cu(IO₃)₂ in pure water.

$$[\text{Cu}^{2+}] = 2.7 \times 10^{-3} \text{ M and } [\text{IO}_3^-] = 5.4 \times 10^{-3}$$

$$K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (2.7 \times 10^{-3})(5.4 \times 10^{-3})^2 = 7.9 \times 10^{-8}$$

a.

	Cu(IO ₃) ₂ (s)	⇌	Cu ²⁺ (aq) +	2 IO ₃ ⁻ (aq)
[] _i			0	0.35
[] _{eq}			x	0.35 + 2x

$$K_{sp} = 7.9 \times 10^{-8} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (x)(0.35 + 2x)^2$$

Assume $2x \ll 0.35$

$$7.9 \times 10^{-8} \approx (x)(0.35)^2 = 0.1225x$$

$$\text{molar solubility} = x = \frac{7.9 \times 10^{-8}}{0.1225} = 6.4 \times 10^{-7} M$$

b.

$\text{Cu}(\text{IO}_3)_2 (\text{s})$	\rightleftharpoons	$\text{Cu}^{2+} (\text{aq})$	+	$2 \text{IO}_3^- (\text{aq})$
$[\]_i$		0.35		0
$[\]_{\text{eq}}$		$0.35 + x$		$2x$

$$K_{\text{sp}} = 7.9 \times 10^{-8} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (0.35 + x)(2x)^2$$

Assume $x \ll 0.35$

$$7.9 \times 10^{-8} \approx (0.35)(2x)^2$$

$$x = \sqrt{\frac{7.9 \times 10^{-8}}{(0.35)(4)}} = 2.4 \times 10^{-4} M$$

$$\text{molar solubility} = x = 2.4 \times 10^{-4} M$$

c. The difference results from the fact that $\text{Cu}(\text{IO}_3)_2$ is a 1:2 electrolyte. The IO_3^- concentration is squared in the solubility product constant expression.

93. a. A precipitate begins to form when $[\text{Pb}^{2+}][\text{I}^-]^2 = K_{\text{sp}} = 6.5 \times 10^{-9}$.

$$[\text{I}^-]^2 = \frac{K_{\text{sp}}}{[\text{Pb}^{2+}]} = \frac{6.5 \times 10^{-9}}{0.0150} = 4.3 \times 10^{-7}$$

$$[\text{I}^-] = \sqrt{4.3 \times 10^{-7}} = 6.6 \times 10^{-4} M$$

$$\text{b. } [\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{I}^-]^2} = \frac{6.5 \times 10^{-9}}{(2.0 \times 10^{-3})^2} = 1.6 \times 10^{-3} M$$

$$\text{percentage of lead remaining in solution} = \frac{1.6 \times 10^{-3}}{0.0150} \times 100 = 11\%$$

95. $[\text{Co}^{2+}] = 5.4 \times 10^{-6} \text{ M}$ and $[\text{OH}^-] = 2(5.4 \times 10^{-6} \text{ M}) = 1.08 \times 10^{-5} \text{ M}$

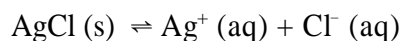
$$K_{\text{sp}} = [\text{Co}^{2+}][\text{OH}^-]^2 = (5.4 \times 10^{-6})(1.08 \times 10^{-5})^2 = 6.3 \times 10^{-16}$$

a. At pH = 10.43, pOH = 3.57 and $[\text{OH}^-] = 10^{-3.57} = 2.7 \times 10^{-4} \text{ M}$

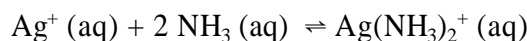
$$\text{solubility} = [\text{Co}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} = \frac{6.3 \times 10^{-16}}{(2.7 \times 10^{-4})^2} = 8.6 \times 10^{-9} \text{ M}$$

b. This is a manifestation of the common-ion effect where the solubility equilibrium is suppressed by another source of one of the ions taking part in the equilibrium.

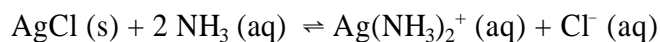
97. a. This equation is merely the sum of the solubility equilibrium and the complex formation equilibrium.



$$K = K_{\text{sp}} = 1.8 \times 10^{-10}$$



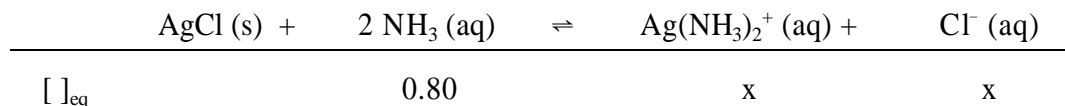
$$K = K_{\text{f}} = 1.7 \times 10^7$$



$$K = K_{\text{sp}}K_{\text{f}} = 3.1 \times 10^{-3}$$

So its equilibrium constant is the product of K_{sp} and K_{f}

b.



$$K_{\text{c}} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{x^2}{(0.80)^2} = 3.1 \times 10^{-3}$$

$$x = \sqrt{(3.1 \times 10^{-3})(0.80)^2} = 4.4 \times 10^{-2} \text{ M} = [\text{Ag}(\text{NH}_3)_2^+] = [\text{Cl}^-]$$

$$4.4 \times 10^{-2} \text{ M} \times 1.00 \text{ L} = 4.4 \times 10^{-2} \text{ mol Cl}^- = 4.4 \times 10^{-2} \text{ mol AgCl dissolved}$$

$$4.4 \times 10^{-2} \text{ mol Ag}(\text{NH}_3)_2^+ \times \frac{2 \text{ mol NH}_3}{1 \text{ mol Ag}(\text{NH}_3)_2^+} = 8.8 \times 10^{-2} \text{ mol NH}_3 \text{ used}$$

$$\text{Initial moles of NH}_3 = 0.80 \text{ M} \times 1.00 \text{ L} + 0.088 \text{ mol} = 0.89 \text{ mol NH}_3$$

$$99. \quad 26.7 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g}} = 0.499 \text{ mol NH}_4\text{Cl}$$

$$a. \quad [\text{NH}_4^+] = \frac{0.499 \text{ mol}}{1.00 \text{ L}} = 0.499 \text{ M}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log (8.42) = 10.19$$

$$\text{pOH} = 3.81 \quad [\text{OH}^-] = 10^{-3.81} = 1.5 \times 10^{-4} \text{ M}$$

b. The concentration of Mg^{2+} in equilibrium with solid $\text{Mg}(\text{OH})_2$ is given by:

$$[\text{Mg}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{1.8 \times 10^{-11}}{(1.5 \times 10^{-4})^2} = 8.0 \times 10^{-4} \text{ M}$$

The percentage of Mg^{2+} removed from solution is:

$$\frac{(0.075 - 8.0 \times 10^{-4}) \text{ mol}}{0.075 \text{ mol}} \times 100 = 99\%$$