

Solutions for Gravimetric Analysis Exercises

1. The terms in a reaction quotient are actually dimensionless ratios of actual concentrations (or pressures) divided by standard concentrations (or pressures). The standard state for solutes is a 1 M solution and for gases it is a pressure of 1 bar (~ 1 atm), so these are the units used. For liquids and solids the standard state is the pure substance, so these ratios are unity. The solvent in a dilute solution is approximated as a pure substance.

2. The equilibrium constant for a reaction is dimensionless because it equals the reaction quotient at equilibrium, and, as discussed in Problem 1, this ratio involves only dimensionless terms.

3. a) Adding the two equations together gives

(1)	$\text{AgCl(s)} \rightleftharpoons \text{Ag}^{\text{+}}(\text{aq}) + \text{Cl}^{\text{-}}(\text{aq})$	$K_1 = 1.8 \times 10^{-10}$
(2)	$\text{Ag}^{\text{+}}(\text{aq}) + \text{Cl}^{\text{-}}(\text{aq}) \rightleftharpoons \text{AgCl(aq)}$	$K_2 = 2.0 \times 10^3$
(3)	$\text{AgCl(s)} \rightleftharpoons \text{AgCl(aq)}$	$K_3 = K_1 \cdot K_2 = 3.6 \times 10^{-7}$

- b) At equilibrium $K_3 = [\text{AgCl(aq)}]$, so $[\text{AgCl(aq)}] = 3.6 \times 10^{-7} \text{ M}$.

4. Determine the solubility of $\text{La}(\text{IO}_3)_3$ using K_{sp} for $\text{La}(\text{IO}_3)_3$ and a table of initial and equilibrium concentration terms.

	$\text{La}(\text{IO}_3)_3(\text{s})$	\rightleftharpoons	$\text{La}^{3+}(\text{aq})$	$+$	$3\text{IO}_3^{\text{-}}(\text{aq})$
init	0		0		0.050
equil	x		x		$0.050 + 3x$

where x equals the increase in the $[\text{La}^{3+}]$ as a result of the dissolving process.

$$\text{at equil, } K_{\text{sp}} = 1.0 \times 10^{-11} = [\text{La}^{3+}][\text{IO}_3^{\text{-}}]^3 = (x)(0.050 + 3x)^3 \approx (x)(0.050)^3$$

\downarrow
 assumes $3x \ll 0.050$

$$[\text{La}^{3+}] = \frac{1.0 \times 10^{-11}}{(0.050)^3} = 8.0 \times 10^{-8} \text{ M} \quad (\text{assumption valid})$$

Solutions for Gravimetric Analysis Exercises

5. MgCO_3 should be more soluble because it has the larger K_{sp} and the stoichiometry of the two salts is the same. If the stoichiometry of the salts is different, one cannot simply compare values of K_{sp} .
6. If only 1% of 0.010 M Ce^{3+} remains in solution this means $[\text{Ce}^{3+}] = 0.00010 \text{ M}$. The concentration of oxalate in equilibrium with 0.00010 M Ce^{3+} is determined by

$$K_{\text{sp}} = 3 \times 10^{-29} = [\text{Ce}^{3+}]^2[\text{C}_2\text{O}_4^{2-}]^3 = (0.00010)^2[\text{C}_2\text{O}_4^{2-}]^3$$

$$[\text{C}_2\text{O}_4^{2-}] = \left(\frac{3 \times 10^{-29}}{(0.00010)^2} \right)^{1/3} = 1.4 \times 10^{-7}$$

To see if this oxalate concentration will precipitate 0.010 M Ca^{2+} , calculate Q for the dissolution of CaC_2O_4 and compare to K_{sp} .

$$Q = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (0.010)(1.4 \times 10^{-7}) = 1.4 \times 10^{-9}$$

Since $Q < K_{\text{sp}}$ ($=1.3 \times 10^{-8}$) for CaC_2O_4 , Ca^{2+} will not precipitate.

7. A high relative supersaturation results in a precipitate with very small particle size and one that is more difficult to recover quantitatively.
8. To lower the relative supersaturation,
- ◆ precipitate from dilute solution
 - ◆ add precipitating agent slowly, with stirring
 - ◆ precipitate from hot solutions
 - ◆ adjust solvent to increase the precipitate solubility
9. An electrolyte in the wash solution preserves the electric double layer and prevents peptization (break up of the precipitate).
10. HNO_3 will volatilize during the drying process, NaNO_3 will not.

Solutions for Gravimetric Analysis Exercises

11.

Salt	At equilibrium	[Ag ⁺] at equilibrium for 0.10 M anion
AgCl	$K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-]$	$1.8 \times 10^{-9} \text{ M}$
AgBr	$K_{sp} = 5.0 \times 10^{-13} = [Ag^+][Br^-]$	$5.0 \times 10^{-12} \text{ M}$
AgI	$K_{sp} = 8.3 \times 10^{-17} = [Ag^+][I^-]$	$8.3 \times 10^{-16} \text{ M}$
Ag ₂ CrO ₄	$K_{sp} = 1.2 \times 10^{-12} = [Ag^+]^2[CrO_4^{2-}]$	$3.5 \times 10^{-6} \text{ M}$

Precipitation occurs when $Q > K_{sp}$. If the mole ratio of Ag⁺ to the anion is the same, then the anions precipitate in order of increasing K_{sp} . Since this is not the case, the salt that needs the smallest [Ag⁺] to reach $Q > K_{sp}$ will precipitate first, followed by the others in order of increasing [Ag⁺]. Based on the information in the above table, I⁻ will precipitate first followed by Br⁻, then Cl⁻ and finally CrO₄²⁻.

12.

$$\frac{0.264 \text{ g Fe}_2\text{O}_3}{2.998 \text{ g powder}} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.69 \text{ g Fe}_2\text{O}_3} \times \frac{2 \text{ mol FeSO}_4 \cdot 7\text{H}_2\text{O}}{1 \text{ mol Fe}_2\text{O}_3} \times \frac{278.01 \text{ g FeSO}_4 \cdot 7\text{H}_2\text{O}}{1 \text{ mol FeSO}_4 \cdot 7\text{H}_2\text{O}} \times \frac{22.131 \text{ g powder}}{20.0 \text{ tablets}} = \frac{0.339 \text{ g FeSO}_4 \cdot 7\text{H}_2\text{O}}{\text{tablet}}$$

13. Let x = grams of K₂SO₄ and y = grams of (NH₄)₂SO₄. Thus, $x + y = 0.649 \text{ g}$.

Since there is one mole of SO₄²⁻ in each mole of reactant and product,

$$\begin{aligned} \text{mol K}_2\text{SO}_4 + \text{mol (NH}_4)_2\text{SO}_4 &= \text{mol BaSO}_4 \\ \frac{x \text{ g K}_2\text{SO}_4}{174.27 \text{ g K}_2\text{SO}_4} + \frac{y \text{ g (NH}_4)_2\text{SO}_4}{132.14 \text{ g (NH}_4)_2\text{SO}_4} &= \frac{0.977 \text{ g BaSO}_4}{233.39 \text{ g BaSO}_4} \end{aligned}$$

Substituting $y = 0.649 - x$ into the above equation and solving for x yields $x = 0.397 \text{ g}$. Therefore,

$$\text{mass \% K}_2\text{SO}_4 = \frac{0.397 \text{ g K}_2\text{SO}_4}{0.649 \text{ g sample}} \times 100 = 61.2\%$$