

REVIEW QUESTIONS

Chapter 16

1. A buffer is prepared by adding 20.0 g of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) and 20.0 g of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) in enough water to prepare 2.00 L of solution. Calculate the pH of this buffer? ($K_a = 1.8 \times 10^{-5}$)

$$20.0 \text{ g HAc} \times \frac{1 \text{ mol}}{60.0 \text{ g}} \times \frac{1}{2.00 \text{ L}} = 0.167 \text{ M} \quad 20.0 \text{ g NaAc} \times \frac{1 \text{ mol}}{82.0 \text{ g}} \times \frac{1}{2.00 \text{ L}} = 0.122 \text{ M}$$

	$\text{HC}_2\text{H}_3\text{O}_2$	+	H_2O	\rightleftharpoons	H_3O^+	+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	0.167		-----		0		0.122
Δ	-x		-----		+x		+x
Equil.	0.167 - x		-----		x		0.122 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(0.122 + x)}{0.167 - x} = 1.8 \times 10^{-5}$$

$$x = \frac{(0.167)(1.8 \times 10^{-5})}{0.122} = 2.46 \times 10^{-5} \quad \text{pH} = -\log(2.46 \times 10^{-5}) = 4.61$$

2. What is the ratio of HCO_3^- to H_2CO_3 in blood of pH 7.4? (K_a for $\text{H}_2\text{CO}_3 = 4.3 \times 10^{-7}$)



$$\text{pH} = \text{p}K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad 7.4 = 6.37 + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \text{antilog}(7.4 - 6.37) = 10^{1.03} = 11$$

3. How many grams of NaBrO should be added to 1.00 L of 0.200 M HBrO to form a buffer with a pH of 8.80? (K_a for HBrO = 2.5×10^{-9})



$$\text{pH} = \text{p}K_a + \log \frac{[\text{BrO}^-]}{[\text{HBrO}]} \quad 8.80 = 8.60 + \log \frac{[\text{BrO}^-]}{[\text{HBrO}]}$$

$$\frac{[\text{BrO}^-]}{[\text{HBrO}]} = \text{antilog}(8.80 - 8.60) = 10^{0.20} = 1.6$$

$$[\text{BrO}^-] = 1.6 (0.200 \text{ M}) = 0.32 \text{ M} \quad 1.00 \text{ L} \times \frac{0.32 \text{ mol}}{1 \text{ L}} \times \frac{118.9 \text{ g}}{1 \text{ mol}} = 38 \text{ g}$$

4. Acetylsalicylic acid (aspirin, $\text{HC}_9\text{H}_7\text{O}_4$) is a weak acid with $K_a = 2.75 \times 10^{-5}$ at 25°C . 3.00 g of sodium acetylsalicylate ($\text{NaC}_9\text{H}_7\text{O}_4$) is added to 200.0 mL of 0.100 M solution of this acid. Calculate the pH of the resulting solution at 25°C .

$$\text{Molarity of NaC}_9\text{H}_7\text{O}_4 = 3.00 \text{ g} \times \frac{1 \text{ mol}}{202 \text{ g}} \times \frac{1}{0.200 \text{ L}} = 0.0743 \text{ M}$$

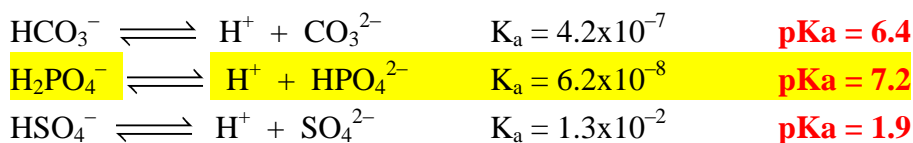
	$\text{HC}_9\text{H}_7\text{O}_4$	+	H_2O	\rightleftharpoons	H_3O^+	+	$\text{C}_9\text{H}_7\text{O}_4^-$
Initial	0.100		-----		0		0.0743
Δ	-x		-----		+x		+x
Equil.	0.100 - x		-----		x		0.0743 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]} = \frac{(x)(0.0743 + x)}{0.100 - x} = 2.75 \times 10^{-5}$$

$$x = \frac{(0.100)(2.75 \times 10^{-5})}{0.0743} = 3.70 \times 10^{-5}$$

$$\text{pH} = -\log(3.70 \times 10^{-5}) = 4.432$$

5. The equations and dissociation constants for three different acids are given below:



Identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. Clearly explain your choice.

The best conjugate pair would be H_2PO_4^- and HPO_4^{2-}
 The $\text{pH} = \text{pKa} = 7.2$ for this buffer when $[\text{H}_2\text{PO}_4^-] = [\text{HPO}_4^{2-}]$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

6. A sample of 25.0 mL of 0.100 M solution of HBr is titrated with 0.200 M NaOH. Calculate the pH of solution after 10.0 mL of the base is added.

	HBr	+ NaOH	→ NaBr	+ H ₂ O
Initial	2.50 mmol	2.00 mmol	0	----
Δ	-2.00 mmol	-2.00 mmol	+2.00 mmol	----
Final	0.50 mmol	0	2.00 mmol	----

$$[\text{H}^+] = [\text{HBr}] = \frac{0.50 \text{ mmol}}{35.0 \text{ mL}} = 0.0143 \text{ M} \quad \text{pH} = -\log(0.0143) = 1.85$$

7. A buffer solution is prepared by adding 0.10 L of 2.0 M acetic acid solution to 0.10 L of 1.0 M NaOH solution.

a) Calculate the pH of this buffer solution.

$$0.10 \text{ L} \times \frac{2.0 \text{ mol}}{1 \text{ L}} = 0.20 \text{ mol HC}_2\text{H}_3\text{O}_2$$

$$0.10 \text{ L} \times \frac{1.0 \text{ mol}}{1 \text{ L}} = 0.10 \text{ mol NaOH}$$

	HC ₂ H ₃ O ₂	+ NaOH	→ NaC ₂ H ₃ O ₂	+ H ₂ O
Initial	0.20	0.10	0	----
Δ	-0.10	-0.10	+0.10	----
Final	0.10	0	0.10	----

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.10 \text{ mol}}{0.20 \text{ L}} = 0.50 \text{ M} \quad [\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.10 \text{ mol}}{0.2 \text{ L}} = 0.50 \text{ M}$$

$$\text{pH} = \text{pKa} + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$\text{From textbook } K_a = 1.7 \times 10^{-5} \quad \text{pKa} = 4.77$$

$$\text{pH} = 4.77 + \log \frac{0.50}{0.50} = 4.77$$

- b) 0.10 L of 0.20 M HCl is added to 0.40 L of the buffer solution above. What is the pH of the resulting solution?

The H_3O^+ ions provided by HCl react with the acetate ions in the buffer.

$$[\text{H}_3\text{O}^+] = (0.10\text{L})(0.20\text{ M}) = 0.020\text{ mol}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2] = (0.40\text{ L})(0.50\text{ M}) = 0.20\text{ mol}$$

	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_3O^+	\rightarrow	$\text{HC}_2\text{H}_3\text{O}_2$	+	H_2O
Initial	0.20		0.020		0.20		----
Δ	-0.020		-0.020		+0.020		----
Final	0.18		0		0.22		----

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.18\text{ mol}}{0.50\text{ L}} = 0.36\text{ M} \quad [\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.22\text{ mol}}{0.50\text{ L}} = 0.44\text{ M}$$

$$\text{pH} = \text{pKa} + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \quad \text{From textbook } \text{Ka} = 1.7 \times 10^{-5}$$

$$\text{pKa} = 4.77 \quad \text{pH} = 4.77 + \log \frac{0.36}{0.44} = 4.68$$

8. A 10.0 mL solution of 0.100 M NH_3 ($K_b = 1.8 \times 10^{-5}$) is titrated with a 0.100 M HCl solution. Calculate the pH of this solution at equivalence point.

$$\text{At equivalence point } 10.0\text{ mL } \text{NH}_3 \times \frac{0.100\text{ mol}}{1\text{ L}} \times \frac{1\text{ HCl}}{1\text{ NH}_3} \times \frac{1\text{ L}}{0.100\text{ mol}} = 10.0\text{ mL of HCl}$$

At equivalence point all NH_3 (1.00 mmol) reacts with all HCl (1.00 mmol) to produce 1.00 mmol of NH_4Cl . Since only salt is present at this point, the pH of solution is based on hydrolysis of this salt.

$$[\text{NH}_4^+] = \frac{1.00\text{ mmol}}{20.0\text{ mL}} = 0.0500\text{ M}$$

	NH_4^+	+	H_2O	\rightleftharpoons	NH_3	+	H_3O^+
Initial	0.0500		----		0		0
Δ	-x		----		+x		+x
Equil.	0.0500-x		----		x		x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.050 - x} = 5.6 \times 10^{-10}$$

$$[\text{H}_3\text{O}^+] = x = \sqrt{(0.050)(5.6 \times 10^{-10})} = 5.3 \times 10^{-6} \quad \text{pH} = -\log(5.3 \times 10^{-6}) = 5.28$$

9. A 10.0-mL solution of 0.300 M NH_3 is titrated with a 0.100 M HCl solution. Calculate the pH after the following additions of the HCl solution: (a) 0.0 mL, (b) 10.0 mL, (c) 30.0 mL
a) Since no acid has been added, the pH of solution is based on the ionization of NH_3 .



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{0.300 - x} = 1.8 \times 10^{-5} \quad x = [\text{OH}^-] = \sqrt{(0.300)(1.8 \times 10^{-5})} = 2.32 \times 10^{-3}$$

$$\text{pOH} = -\log(2.32 \times 10^{-3}) = 2.63 \quad \text{pH} = 14.00 - 2.63 = 11.37$$

- b) Addition of 10.0 mL of acid neutralizes some of the ammonia, as shown below:**

	NH_3	+	HCl	\rightarrow	NH_4^+	+	Cl^-
Initial	3.00 mmol		1.00 mmol		0		----
Δ	-1.00 mmol		-1.00 mmol		+1.00 mmol		----
Final	2.00 mmol		0		1.00 mmol		----

$$[\text{NH}_3] = \frac{2.00 \text{ mmol}}{20.0 \text{ mL}} = 0.100 \text{ M} \quad [\text{NH}_4^+] = \frac{1.00 \text{ mmol}}{20.0 \text{ mL}} = 0.0500 \text{ M}$$

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \quad \text{p}K_a = \log K_a = 9.25$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 9.25 + \log \frac{0.100}{0.0500} = 9.55$$

- c) After addition of 30.0 mL of HCl equivalence point is reached. At this point all NH_3 (3.00 mmol) reacts with all HCl (3.00 mmol) to produce 3.00 mmol of NH_4Cl . Since only salt is present at this point, the pH of solution is based on hydrolysis of this salt.**

$$[\text{NH}_4^+] = \frac{3.00 \text{ mmol}}{40.0 \text{ mL}} = 0.0750 \text{ M}$$

	NH_4^+	+	H_2O	\rightleftharpoons	NH_3	+	H_3O^+
Initial	0.0750		----		0		0
Δ	-x		----		+x		+x
Equil.	0.0750-x		----		x		x

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(x)(x)}{(0.0750 - x)} = 5.56 \times 10^{-10}$$

$$x = [\text{H}_3\text{O}^+] = \sqrt{(0.0750)(5.56 \times 10^{-10})} = 6.46 \times 10^{-6} \quad \text{pH} = -\log(6.46 \times 10^{-6}) = 5.19$$

10. A 45.0-mL sample of 0.200 M acetic acid is titrated with 0.180 M NaOH. Calculate the pH of the solution (a) before addition of NaOH, (b) after addition of 20.0 mL of NaOH and (c) at the equivalence point.

a) Since no base has been added, the pH of solution is based on the ionization of acid.



$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{0.200 - x} = 1.7 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = \sqrt{(0.200)(1.7 \times 10^{-5})} = 1.84 \times 10^{-3} \quad \text{pH} = -\log(1.84 \times 10^{-3}) = 2.73$$

b) Addition of 20.0 mL of NaOH neutralizes some of the acetic acid, as shown below:

	$\text{HC}_2\text{H}_3\text{O}_2$	+ NaOH	\rightarrow	$\text{NaC}_2\text{H}_3\text{O}_2$	+ H_2O
Initial	9.00 mmol	3.60 mmol		0	----
Δ	-3.60 mmol	-3.60 mmol		+3.60 mmol	----
Final	5.40 mmol	0		3.60 mmol	----

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{5.40 \text{ mmol}}{65.0 \text{ mL}} = 0.0831 \text{ M} \quad [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{3.60 \text{ mmol}}{65.0 \text{ mL}} = 0.0554 \text{ M}$$

$$K_a = 1.7 \times 10^{-5} \quad \text{p}K_a = \log K_a = 4.77 \quad \text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.77 + \log \frac{0.0554}{0.0831} = 4.59$$

c) At equivalence point:

$$45.0 \text{ mL acid} \times \frac{0.200 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mol base}}{1 \text{ mol acid}} \times \frac{1 \text{ L}}{0.180 \text{ mol}} = 50.0 \text{ mL of base}$$

At this point all the acid (9.00 mmol) is neutralized by the base (9.00 mmol) to produce 9.00 mmol of salt. Since only salt is present, the pH of the solution is based on hydrolysis of this salt.

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{9.00 \text{ mmol}}{95.0 \text{ mL}} = 0.09474 \text{ M}$$

	$\text{C}_2\text{H}_3\text{O}_2^-$	+ H_2O	\rightleftharpoons	$\text{HC}_2\text{H}_3\text{O}_2$	+ OH^-
Initial	0.09474	----		0	0
Δ	-x	----		+x	+x
Equil.	0.09474-x	----		x	x

$$K_b = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$$

$$K_b = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{OH}^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{(0.09474 - x)} = 5.88 \times 10^{-10}$$

$$x = [\text{OH}^-] = \sqrt{(0.09474)(5.88 \times 10^{-10})} = 7.47 \times 10^{-6}$$

$$\text{pOH} = -\log(7.47 \times 10^{-6}) = 5.13$$

$$\text{pH} = 14.00 - 5.13 = 8.87$$

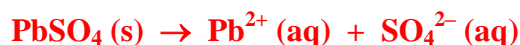
11. Calculate the molar solubility of AgBr ($K_{sp} = 5.0 \times 10^{-13}$) in 0.50 M NaBr solution.

	AgBr (s)	→	Ag⁺ (aq) +	Br⁻ (aq)
Initial	----		0	0.50
Δ	-x		+x	+x
Final	-----		x	0.50 + x

$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = (x)(0.50 + x) = 5.0 \times 10^{-13}$$

$$\text{solubility} = x = \frac{5.0 \times 10^{-13}}{0.50} = 1.0 \times 10^{-12} \text{ M}$$

12. A solution is made by mixing 10.0 mL of 0.10 M Pb(NO₃)₂ and 10.0 mL of 0.0010 M Na₂SO₄. Will a precipitate form? (K_{sp} for PbSO₄ = 1.06×10^{-8})



$$[\text{Pb}^{2+}] = \frac{(0.10 \text{ M})(10.0 \text{ mL})}{(20.0 \text{ mL})} = 0.0500 \text{ M} \quad [\text{SO}_4^{2-}] = \frac{(0.0010 \text{ M})(10.0 \text{ mL})}{(20.0 \text{ mL})} = 5.00 \times 10^{-4} \text{ M}$$

$$Q_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (0.0500)(5.00 \times 10^{-4}) = 2.50 \times 10^{-5}$$

Since $Q_{sp} > K_{sp}$, precipitation will occur

13. The solubility of iron (II) hydroxide, Fe(OH)₂, is 1.43×10^{-3} g/L.
a) Calculate the K_{sp} for iron (II) hydroxide.



$$[\text{Fe}^{2+}] = [\text{Fe}(\text{OH})_2] = \frac{1.43 \times 10^{-3} \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{89.85 \text{ g}} = 1.59 \times 10^{-5} \text{ M}$$

$$[\text{OH}^-] = 2 (1.59 \times 10^{-5}) = 3.18 \times 10^{-5} \text{ M}$$

$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = (1.59 \times 10^{-5})(3.18 \times 10^{-5})^2 = 1.61 \times 10^{-14}$$

- b) Calculate pH of a saturated solution of iron (II) hydroxide.

$$\text{From part (a)} \quad [\text{OH}^-] = 3.18 \times 10^{-5} \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.18 \times 10^{-5}} = 3.14 \times 10^{-10} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = 9.50$$

- c) A 50.0 mL sample of 3.00×10^{-3} M FeSO_4 solution is added to 50.0 mL of 4.00×10^{-6} M NaOH solution. Does a precipitate form?

$$[\text{Fe}^{2+}] = \frac{(3.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{(100.0 \text{ mL})} = 1.50 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = \frac{(4.00 \times 10^{-6} \text{ M})(50.0 \text{ mL})}{(100.0 \text{ mL})} = 2.00 \times 10^{-6} \text{ M}$$

$$Q_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2 = (1.50 \times 10^{-3})(2.00 \times 10^{-6})^2 = 6.00 \times 10^{-15}$$

Since $Q_{\text{sp}} < K_{\text{sp}}$, precipitation will not occur

14. Lead iodate, $\text{Pb}(\text{IO}_3)_2$, is a slightly soluble salt with a K_{sp} of 2.6×10^{-13} at 25°C . To 35.0 mL of 0.150 M $\text{Pb}(\text{NO}_3)_2$ solution is added 15.0 mL of 0.800 M KIO_3 . A precipitate of $\text{Pb}(\text{IO}_3)_2$ results. What are the $[\text{Pb}^{2+}]$ and $[\text{IO}_3^-]$ in the final solution?

$$[\text{Pb}^{2+}] = \frac{(0.150 \text{ M})(35.0 \text{ mL})}{(50.0 \text{ mL})} = 0.105 \text{ M} \quad [\text{IO}_3^-] = \frac{(0.800 \text{ M})(15.0 \text{ mL})}{(50.0 \text{ mL})} = 0.240 \text{ M}$$

Using bounce-back method, first assume all Pb^{2+} reacts with all IO_3^- ion to produce $\text{Pb}(\text{IO}_3)_2$, and then some of the precipitate dissolves back to the ions.

	$\text{Pb}(\text{IO}_3)_2$ (s)	\rightarrow	Pb^{2+} (aq) +	2IO_3^- (aq)
Initial	----		0.105	0.240
Δ_1	+0.105		-0.105	-0.210
Precipitate	-----		0	0.030
Δ_2	-x		+x	+2x
Finish	-----		x	0.030+2x

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = (x)(0.030 + 2x)^2 = 2.6 \times 10^{-13}$$

$$[\text{Pb}^{2+}] = x = \frac{2.6 \times 10^{-13}}{(0.030)^2} = 2.9 \times 10^{-10} \text{ M}$$

$$[\text{IO}_3^-] = 0.030 + 2x = 0.030 \text{ M}$$

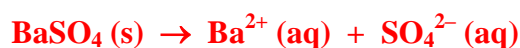
15. Consider a solution that is 0.010 M in Ba^{2+} and 0.020 M in Ca^{2+} . If sodium sulfate is added to this solution to selectively precipitate one of the cations, which will precipitate first? What is the minimum concentration of Na_2SO_4 that would trigger the precipitation of this cation?

From textbook,

$$K_{\text{sp}} \text{ for } \text{BaSO}_4 = 1.07 \times 10^{-10}$$

$$K_{\text{sp}} \text{ for } \text{CaSO}_4 = 7.10 \times 10^{-5}$$

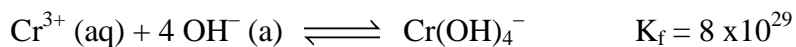
Since the solution stoichiometry for both these compounds are similar, it would be appropriate to relate K_{sp} and molar solubility. Since the lower K_{sp} value would require the lower sulfate ion concentration in order to precipitate, it would then follow that Ba^{2+} would precipitate first.



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.07 \times 10^{-10}$$

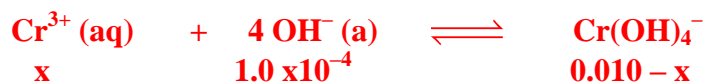
$$[\text{SO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ba}^{2+}]} = \frac{1.07 \times 10^{-10}}{0.010 \text{ M}} = 1.07 \times 10^{-8} \text{ M}$$

16. What is the Cr^{3+} concentration when 0.010 mol of $\text{Cr}(\text{NO}_3)_3$ is dissolved in a liter of solution buffered at pH of 10.0. Cr^{3+} forms a complex ion with hydroxide shown below:



$$\text{pOH} = 14.0 - 10.0 = 4.0 \quad [\text{OH}^-] = \text{antilog pOH} = 1.0 \times 10^{-4}$$

Due to the large K_f all of Cr^{3+} is converted to the complex ion, and some subsequently dissociates back to Cr^{3+} . Then at equilibrium,



$$K_f = \frac{[\text{Cr}(\text{OH})_4^-]}{[\text{Cr}^{3+}][\text{OH}^-]^4} = \frac{(0.010 - x)}{x(1.0 \times 10^{-4})^4} = 8 \times 10^{29}$$

$$[\text{Cr}^{3+}] = x = 1.2 \times 10^{-16} \text{ M}$$

Note: Since the solution is buffered, $[\text{OH}^-]$ will remain constant during the reaction.

17. A 0.10-mol sample of AgNO_3 is dissolved in 1.00 L of 1.00 M NH_3 . If 0.010 mol of NaCl is added to this solution, will AgCl ($K_{\text{sp}} = 1.8 \times 10^{-10}$) precipitate? (Ag^+ and NH_3 form the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ with $K_f = 1.6 \times 10^7$)

To determine if a precipitate forms, we need to determine the concentration of Ag^+ in the solution, and then calculate Q_{sp} to determine if a precipitate forms.

To determine the concentration of Ag^+ , due to the large K_f value, assume all of the Ag^+ reacts to form the complex and then some dissociates back.

	$\text{Ag}^+ (\text{aq})$	$+ 2 \text{NH}_3 (\text{aq})$	\rightarrow	$\text{Ag}(\text{NH}_3)_2^+ (\text{aq})$
Initial	0.10	1.00		0
Δ_1	-0.10	-0.20		+0.10
Complex	0	0.80		0.10
Δ_2	+x	+2x		-x
Finish	x	0.80+2x		0.10-x

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{(0.10 - x)}{x(0.80 + 2x)^2} = 1.6 \times 10^7$$

$$[\text{Ag}^+] = x = \frac{0.20}{(0.80)^2(1.6 \times 10^7)} = 9.8 \times 10^{-9} \text{ M}$$

$$Q_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (9.8 \times 10^{-9})(0.010) = 9.8 \times 10^{-11} < 1.8 \times 10^{-10}$$

AgCl will NOT precipitate

18. AgNO_3 is added to a solution that is 0.10 M in NaCl and 0.010 M K_2CrO_4 . Assume no dilution caused by the addition of AgNO_3 . Given the K_{sp} values below:

$$K_{sp} \text{ for } \text{AgCl} = 1.6 \times 10^{-10}$$

$$K_{sp} \text{ for } \text{Ag}_2\text{CrO}_4 = 9.0 \times 10^{-12}$$

- a) Which precipitates first, AgCl or Ag_2CrO_4 ? Calculate the $[\text{Ag}^+]$ when precipitation first begins.

Since the solution stoichiometry for both these compounds are not the same, it would not be appropriate to relate K_{sp} and molar solubility.

To determine which ion precipitates first, we must calculate the cation concentration required for each precipitation. The lower value required for precipitation would indicate the ion that would precipitate first.

$[\text{Ag}^+]$ required for AgCl precipitation:



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.6 \times 10^{-10}}{0.10 \text{ M}} = 1.6 \times 10^{-9} \text{ M}$$

$[\text{Ag}^+]$ required for Ag_2CrO_4 precipitation:



$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 9.0 \times 10^{-12}$$

$$[\text{Ag}^+] = \sqrt{\frac{K_{sp}}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{9.0 \times 10^{-12}}{0.010 \text{ M}}} = 3.0 \times 10^{-5} \text{ M}$$

The precipitation occurs for the salt which requires the smallest $[\text{Ag}^+]$ at equilibrium. Therefore **AgCl precipitates first at a $[\text{Ag}^+]$ of $1.6 \times 10^{-9} \text{ M}$**

- b) What is the $[\text{Cl}^-]$ when Ag_2CrO_4 first begins to precipitate?

Calculations above show that in order of Ag_2CrO_4 to precipitate, the $[\text{Ag}^+]$ must equal $3.0 \times 10^{-5} \text{ M}$. Therefore,

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (3.0 \times 10^{-5}) [\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$[\text{Cl}^-] = \frac{1.6 \times 10^{-10}}{3.0 \times 10^{-5}} = 5.3 \times 10^{-6} \text{ M}$$