REVIEW QUESTIONS
Chapter 17

1. A buffer is prepared by adding 20.0 g of acetic acid ($HC_2H_3O_2$) and 20.0 g of sodium acetate ($NaC_2H_3O_2$) in enough water to prepare 2.00 L of solution. Calculate the pH of this buffer? ($K_a = 1.8 \times 10^{-5}$)

$$HC_2H_3O_2 \;+\; H_2O \;\rightleftharpoons\; H_3O^+ \;+\; C_2H_3O_2^-$$

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

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 4.74 + \log\frac{0.122\;M}{0.167\;M}$$

$$pH = 4.74 - 0.136 = 4.60$$

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

$$H_2CO_3 \;+\; H_2O \;\rightleftharpoons\; H_3O^+ \;+\; HCO_3^-$$

$$pH = pK_a + \log\frac{[HCO_3^-]}{[H_2CO_3]} \qquad 7.4 = 6.37 + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \text{antilog}\,(7.4 - 6.37) = 10^{1.03} = 11$$

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 $= 2.5 \times 10^{-9}$)

$$HBrO \;+\; H_2O \;\rightleftharpoons\; H_3O^+ \;+\; BrO^-$$

$$pH = pK_a + \log\frac{[BrO^-]}{[HBrO]} \qquad 8.80 = 8.60 + \log\frac{[BrO^-]}{[HBrO]}$$

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

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

4. Acetylsalicylic acid (aspirin, $HC_9H_7O_4$) is a weak acid with $Ka = 2.75 \times 10^{-5}$ at 25°C. 3.00 g of sodium acetylsalicylate ($NaC_9H_7O_4$) is added to 200.0 mL of 0.100 M solution of this acid. Calculate the pH of the resulting solution at 25°C.

$$HC_9H_7O_4 \; + \; H_2O \; \rightleftharpoons \; H_3O^+ + \; C_9H_7O_4^-$$

$$[NaC_9H_7O_4] = 3.00 \text{ g} \times \frac{1 \text{ mol}}{202 \text{ g}} \times \frac{1}{0.200 \text{ L}} = 0.0743 \text{ M}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = 4.56 + \log \frac{0.0743 \text{ M}}{0.100 \text{ M}}$$

$$pH = 4.56 - 0.129 = 4.43$$

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

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$		$K_a = 4.2 \times 10^{-7}$	**pKa = 6.4**
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$		$K_a = 6.2 \times 10^{-8}$	**pKa = 7.2**
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$		$K_a = 1.3 \times 10^{-2}$	**pKa = 1.9**

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 pH = pKa = 7.2 for this buffer when $[H_2PO_4^-] = [HPO_4^{2-}]$

$$pH = pK_a + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

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	+	H₂O
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		----

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

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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.

$$0.10 \ \cancel{L} \times \frac{2.0 \ mol}{1 \ \cancel{L}} = 0.20 \ mol \ HC_2H_3O_2$$

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

	$HC_2H_3O_2$	+	NaOH	$\rightarrow$	$NaC_2H_3O_2$ +	H_2O
Initial	0.20		0.10		0	----
Δ	−0.10		−0.10		+0.10	----
Final	0.10		0		0.10	----

$$[C_2H_3O_2^-] = \frac{0.10 \ mol}{0.20 \ L} = 0.50 \ M \qquad [HC_2H_3O_2] = \frac{0.10 \ mol}{0.2 \ L} = 0.50 \ M$$

$$pH = pKa + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

From textbook $Ka = 1.7 \times 10^{-5}$ $\qquad\qquad$ pKa = 4.77

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

   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.

$$[H_3O^+] = (0.10L)(0.20 \ M) = 0.020 \ mol$$

$$[C_2H_3O_2^-] = [HC_2H_3O_2] = (0.40 \ L)(0.50 \ M) = 0.20 \ mol$$

	$C_2H_3O_2^-$	+	H_3O^+	$\rightarrow$	$HC_2H_3O_2$ +	H_2O
Initial	0.20		0.020		0.20	----
Δ	−0.020		−0.020		+0.020	----
Final	0.18		0		0.22	----

$$[C_2H_3O_2^-] = \frac{0.18 \ mol}{0.50 \ L} = 0.36 \ M \qquad [HC_2H_3O_2] = \frac{0.22 \ mol}{0.50 \ L} = 0.44 \ M$$

$$pH = pKa + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad\qquad \text{From textbook } Ka = 1.7 \times 10^{-5}$$

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

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.

At equivalence point   10.0 mL NH_3 x $\dfrac{0.100 \text{ mol}}{1 \text{ L}}$ x $\dfrac{1 \text{ HCl}}{1 \text{ NH}_3}$ x $\dfrac{1 \text{ L}}{0.100 \text{ mol}}$ = 10.0 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.

$$[NH_4^+] = \dfrac{1.00 \text{ mmol}}{20.0 \text{ mL}} = 0.0500 \text{ M}$$

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

$$K_a = \dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \qquad K_a = \dfrac{[H_3O^+][NH_3]}{[NH_4^+]} = \dfrac{(x)(x)}{0.050 - \cancel{x}} = 5.6 \times 10^{-10}$$

$$[H_3O^+] = x = \sqrt{(0.050)(5.6 \times 10^{-10})} = 5.3 \times 10^{-6} \qquad pH = -\log(5.3 \times 10^{-6}) = 5.28$$

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.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \text{From textbook, } K_b = 1.8 \times 10^{-5}$$

$$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = \dfrac{(x)(x)}{0.300 - \cancel{x}} = 1.8 \times 10^{-5} \qquad x = [OH^-] = \sqrt{(0.300)(1.8 \times 10^{-5})} = 2.\underline{3}2 \times 10^{-3}$$

$$pOH = -\log(2.\underline{3}2 \times 10^{-3}) = 2.63 \qquad pH = 14.00 - 2.63 = 11.37$$

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		----

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$$[NH_3] = \frac{2.00 \text{ mmol}}{20.0 \text{ mL}} = 0.100 \text{ M} \qquad [NH_4^+] = \frac{1.00 \text{ mmol}}{20.0 \text{ mL}} = 0.0500 \text{ M}$$

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}6 \times 10^{-10} \qquad pK_a = \log K_a = 9.25$$

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

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$_4$Cl. Since only salt is present at this point, the pH of solution is based on hydrolysis of this salt.**

$$[NH_4^+] = \frac{3.00 \text{ mmol}}{40.0 \text{ mL}} = 0.0750 \text{ M}$$

	NH$_4^+$	+	H$_2$O	$\rightleftharpoons$	NH$_3$	+	H$_3$O$^+$
Initial	0.0750		----		0		0
Δ	−x		----		+x		+x
Equil.	0.0750–x		----		x		x

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(x)(x)}{(0.0750 - x)} = 5.\underline{5}6 \times 10^{-10}$$

$$x = [H_3O^+] = \sqrt{(0.0750)(5.\underline{5}6 \times 10^{-10})} = 6.\underline{4}6 \times 10^{-6} \qquad pH = -\log(6.\underline{4}6 \times 10^{-6}) = 5.19$$

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.**

$$HC_2H_3O_2 \; + \; H_2O \; \rightleftharpoons \; C_2H_3O_2^- \; + \; H_3O^+ \qquad \text{From textbook, } K_a = 1.7 \times 10^{-5}$$

$$K_a = \frac{[CHO_2^-][H_3O^+]}{[HC_2H_3O_2]} = \frac{(x)(x)}{0.200 - \cancel{x}} = 1.7 \times 10^{-5}$$

$$x = [H_3O^+] = \sqrt{(0.200)(1.7 \times 10^{-5})} = 1.\underline{8}4 \times 10^{-3} \qquad pH = -\log(1.\underline{8}4 \times 10^{-3}) = 2.73$$

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

	$HC_2H_3O_2$ +	NaOH	$\rightarrow$ $NaC_2H_3O_2$ +	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	----

$$[HC_2H O_2] = \frac{5.40 \text{ mmol}}{65.0 \text{ mL}} = 0.0831 \text{ M} \qquad [C_2H_3O_2^-] = \frac{3.60 \text{ mmol}}{65.0 \text{ mL}} = 0.0554 \text{ M}$$

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

   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.

$$[C_2H_3O_2^-] = \frac{9.00 \text{ mmol}}{95.0 \text{ mL}} = 0.094\underline{7}4 \text{ M}$$

	$C_2H_3O_2^-$ +	H_2O	$\rightleftharpoons$ $HC_2H_3O_2$ +	OH^-
Initial	0.094\underline{7}4	----	0	0
Δ	−x	----	+x	+x
Equil.	0.094\underline{7}4–x	----	x	x

$$K_b = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.\underline{8}8 \times 10^{-10} \qquad K_b = \frac{[C_2H_3O_2^-][OH^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{(0.094\underline{7}4 - \cancel{x})} = 5.\underline{8}8 \times 10^{-10}$$

$$x = [OH^-] = \sqrt{(0.094\underline{7}4)(5.\underline{8}8 \times 10^{-10})} = 7.\underline{4}7 \times 10^{-6}$$

$$pOH = -\log(7.\underline{4}7 \times 10^{-6}) = 5.13 \qquad pH = 14.00 - 5.13 = 8.87$$

11. Calculate the molar solubility of AgBr (Ksp= 5.0×10^{-13}) in 0.50 M NaBr solution.

	AgBr (s)	$\rightarrow$	Ag^+ (aq) +	Br^- (aq)
Initial	----		0	0.50
Δ	$-x$		$+x$	$+x$
Final	-----		x	0.50 + x

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

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

12. A solution is made by mixing 10.0 mL of 0.10 M Pb(NO$_3$)$_2$ and 10.0 mL of 0.0010 M Na$_2$SO$_4$. Will a precipitate form? (Ksp for PbSO$_4$ = 1.06×10^{-8})

$$PbSO_4 \text{ (s)} \rightarrow Pb^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)}$$
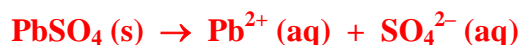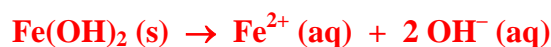
$$[Pb^{2+}] = \frac{(0.10 \text{ M})(10.0 \text{ mL})}{(20.0 \text{ mL})} = 0.0500 \text{ M} \qquad [SO_4^{2-}] = \frac{(0.0010 \text{ M})(10.0 \text{ mL})}{(20.0 \text{ mL})} = 5.00 \times 10^{-4} \text{ M}$$

$$Q_{sp} = [Pb^{2+}][SO_4^{2-}] = (0.0500)(5.00 \times 10^{-4}) = 2.50 \times 10^{-5}$$

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

13. The solubility of iron (II) hydroxide, Fe(OH)$_2$, is 1.43×10^{-3} g/L.
   a) Calculate the Ksp for iron (II) hydroxide.

$$Fe(OH)_2 \text{ (s)} \rightarrow Fe^{2+} \text{ (aq)} + 2 \text{ OH}^- \text{ (aq)}$$

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

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

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

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

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

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

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

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?

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

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

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

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

14. Lead iodate , $Pb(IO_3)_2$, is a slightly soluble salt with a Ksp of 2.6×10^{-13} at 25°C. To 35.0 mL of 0.150 $Pb(NO_3)_2$ solution is added 15.0 mL of 0.800 M KIO_3. A precipitate of $Pb(IO_3)_2$ results. What are the $[Pb^{2+}]$ and $[IO_3^-]$ in the final solution?

$$[Pb^{2+}] = \frac{(0.150 \text{ M})(35.0 \text{ mL})}{(50.0 \text{ mL})} = 0.105 \text{ M} \qquad [IO_3^-] = \frac{(0.800 \text{ M})(15.0 \text{ mL})}{(50.0 \text{ mL})} = 0.240 \text{ M}$$

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

	$Pb(IO_3)_2$ (s)	$\rightarrow$	Pb^{+2} (aq) +	$2 IO_3^-$ (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

$$K_{sp} = [Pb^{2+}][IO_3^-]^2 = (x)(0.030 + \cancel{x})^2 = 2.6 \times 10^{-13}$$

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

$$[IO_3^-] = 0.030 + 2x = 0.030 \text{ M}$$

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,

$$\textbf{K}_{\textbf{sp}} \textbf{ for BaSO}_4 = \textbf{1.07x10}^{-10}$$
$$\textbf{K}_{\textbf{sp}} \textbf{ for CaSO}_4 = \textbf{7.10x10}^{-5}$$

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.

$$\textbf{BaSO}_4 \textbf{ (s)} \rightarrow \textbf{Ba}^{2+} \textbf{ (aq)} + \textbf{SO}_4{}^{2-} \textbf{ (aq)}$$
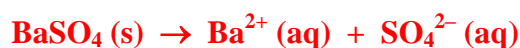
$$\textbf{K}_{\text{sp}} = \textbf{[Ba}^{2+}\textbf{][SO}_4^{2-}\textbf{]} = \textbf{1.07x10}^{-10}$$

$$\textbf{[SO}_4^{2-}\textbf{]} = \frac{\textbf{K}_{\text{sp}}}{\textbf{[Ba}^{2+}\textbf{]}} = \frac{\textbf{1.07x10}^{-10}}{\textbf{0.010 M}} = \textbf{1.07x10}^{-8} \textbf{ M}$$

16. What is the Cr^{3+} concentration when 0.010 mol of $Cr(NO_3)_3$ is dissolved in a liter of solution buffered at pH of 10.0. Cr^{3+} forms a complex ion with hydroxide shown below:

$$Cr^{3+} \text{ (aq)} + 4 \text{ OH}^- \text{ (a)} \rightleftharpoons Cr(OH)_4{}^- \qquad K_f = 8 \text{ x}10^{29}$$

pOH = 14.0 – 10.0 = 4.0   **[OH⁻] = antilog pOH = 1.0 x10^{-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,

$\textbf{Cr}^{3+}$ **(aq)**	**+**	**4 OH⁻ (a)**	$\rightleftharpoons$	$\textbf{Cr(OH)}_4{}^-$
x		**1.0 x10^{-4}**		**0.010 – x**
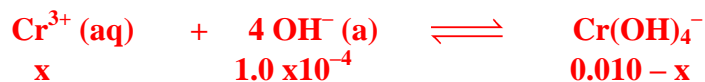
$$\textbf{K}_{\text{f}} = \frac{\textbf{[Cr(OH)}_4^-\textbf{]}}{\textbf{[Cr}^{3+}\textbf{][OH}^-\textbf{]}^4} = \frac{\textbf{(0.010 - x)}}{\textbf{x (1.0x10}^{-4}\textbf{)}^4} = \textbf{8x10}^{29}$$

$$\textbf{[Cr}^{3+}\textbf{]} = \textbf{x} = \textbf{1.2x10}^{-16} \textbf{ M}$$

<u>Note:</u> Since the solution is buffered, [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 ($K_{sp} = 1.8 \times 10^{-10}$) precipitate? ($Ag^+$ and NH_3 form the complex ion $[Ag(NH_3)_2]^+$ 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.

	Ag^+ (aq) +	2 NH_3 (aq) $\rightarrow$	$Ag(NH_3)_2^+$ (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

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{(0.10 - \cancel{x})}{x\,(0.80 + \cancel{2x})^2} = 1.6 \times 10^7$$

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

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

AgCl will NOT precipitate

18. AgNO$_3$ is added to a solution that is 0.10 M in NaCl and 0.010 M K$_2$CrO$_4$. Assume no dilution caused by the addition of AgNO$_3$. Given the Ksp values below:

$$\text{Ksp for AgCl} = 1.6 \times 10^{-10}$$
$$\text{Ksp for Ag}_2\text{CrO}_4 = 9.0 \times 10^{-12}$$

a) Which precipitates first, AgCl or Ag$_2$CrO$_4$? Calculate the [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.

[Ag$^+$] required for AgCl precipitation:

$$\textbf{AgCl (s)} \quad \rightarrow \quad \textbf{Ag}^+ \textbf{ (aq)} + \quad \textbf{Cl}^- \textbf{ (aq)}$$

$$\textbf{K}_{sp} = \textbf{[Ag}^+\textbf{][Cl}^-\textbf{]} = \textbf{1.6x10}^{-10}$$

$$\textbf{[Ag}^+\textbf{]} = \frac{\textbf{K}_{sp}}{\textbf{[Cl}^-\textbf{]}} = \frac{\textbf{1.6x10}^{-10}}{\textbf{0.10 M}} = \textbf{1.6x10}^{-9} \textbf{ M}$$

[Ag$^+$] required for Ag$_2$CrO$_4$ precipitation:

$$\textbf{Ag}_2\textbf{Cr}_4 \textbf{ (s)} \quad \rightarrow \quad \textbf{2 Ag}^+ \textbf{ (aq)} + \quad \textbf{CrO}_4^{2-} \textbf{ (aq)}$$

$$\textbf{K}_{sp} = \textbf{[Ag}^+\textbf{]}^2\textbf{[CrO}_4^{2-}\textbf{]} = \textbf{9.0x10}^{-12}$$

$$\textbf{[Ag}^+\textbf{]} = \sqrt{\frac{\textbf{K}_{sp}}{\textbf{[CrO}_4^{2-}\textbf{]}}} = \sqrt{\frac{\textbf{9.0x10}^{-12}}{\textbf{0.010 M}}} = \textbf{3.0x10}^{-5} \textbf{ M}$$

The precipitation occurs for the salt which requires the smallest [Ag$^+$] at equilibrium. Therefore AgCl precipitates first at a [Ag$^+$] of 1.6x10^{-9} M

b) What is the [Cl$^-$] when Ag$_2$CrO$_4$ first begins to precipitate?

Calculations above show that in order of Ag$_2$CrO$_4$ to precipitate, the [Ag$^+$] must equal 3.0x10^{-5} M. Therefore,

$$\textbf{K}_{sp} = \textbf{[Ag}^+\textbf{][Cl}^-\textbf{]} = \textbf{(3.0x10}^{-5}\textbf{) [Cl}^-\textbf{]} = \textbf{1.6x10}^{-10}$$

$$\textbf{[Cl}^-\textbf{]} = \frac{\textbf{1.6x10}^{-10}}{\textbf{3.0x10}^{-5}} = \textbf{5.3x10}^{-6} \textbf{ M}$$

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19. Blood is buffered by H_2CO_3/HCO_3^- system. Normal blood plasma is 0.024 M HCO_3^- and 0.0012 M H_2CO_3. pK_a for H_2CO_3 at body temperature is 6.1.

a) What is pH of blood plasma?

$$pH = pKa + \log \frac{[base]}{[acid]} \quad 6.1 + \log \frac{0.024}{0.0012} = 7.4$$

b) If the volume of blood in a normal adult is 5.0 L, what mass of HCl can be neutralized by the buffering system in blood before the pH falls below 7.0 (which would result in death)?

For pH to drop by 0.4 to below 7.0, the ratio of base to acid in the buffer must change to 8 (from the current 20). The amount of the components of the buffer in 5.0 L of blood are:

mol HCO_3^- = (5.0 L x 0.024 M) = 0.12 mol
mol H_2CO_3 = (5.0 L x 0.0012 M) = 0.0060 mol

The HCl neutralized by the buffer reacts with HCO_3^- to form H_2CO_3. Therefore, after x-mol HCl is neutralized, the amounts of buffer components will be:

mol HCO_3^- = 0.12 mol – x   **$\dfrac{[base]}{[acid]} = \dfrac{0.12 \text{ -x}}{0.0060 \text{ +x}} = 8$**
mol H_2CO_3 = 0.0060 mol + x

Solving for x (mol HCl neutralized):

x = 0.008 mol HCl x 36.5 g/mol = 0.3 g HCl

c) For the same adult in (b), what mass of NaOH can be neutralized before the pH rises above 7.8?

For pH to rise by 0.4 to above 7.8, the ratio of base to acid in the buffer must change to 50 (from the current 20). The NaOH neutralized by the buffer reacts with H_2CO_3 to form HCO_3^-. Therefore, after x-mol NaOH is neutralized, the amounts of buffer components will be:

mol HCO_3^- = 0.12 mol + x   **$\dfrac{[base]}{[acid]} = \dfrac{0.12 \text{ +x}}{0.0060 \text{ -x}} = 50$**
mol H_2CO_3 = 0.0060 mol – x

Solving for x (mol NaOH neutralized):

x = 0.0035 mol NaOH x 40.0 g/mol = 0.14 g NaOH

20. An important buffer used in biochemical analysis is made by dissolving TRIS [$(HOCH_2)_3CNH_2$] in dilute HCl. A biochemist prepares a buffer by dissolving an unknown amount of TRIS in 1L of 0.095 M HCl solution. The pH of the resulting buffer solution was measured to be 8.53. How many grams of TRIS was used in this buffer? Assume volume of solution did not change after addition of TRIS.
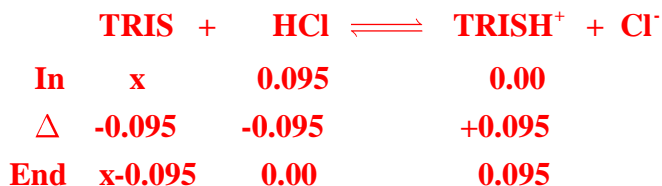(Molar mass of TRIS = 121.14 g/mol; pK_b of TRIS = 5.91)

$$\text{TRIS} + \text{HCl} \rightleftharpoons \text{TRISH}^+ + \text{Cl}^-$$

$$pK_a = 14.00 - 5.91 = 8.09$$

$$pH = pK_a + \log \frac{[\text{TRIS}]}{[\text{TRISH}^+]}$$

$$\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 10^{pH - pKa} = 10^{0.44} = 2.75$$

In order to prepare the buffer, all the HCl in solution must react with added TRIS to form the conjugate acid and leave excess TRIS as the weak base. Therefore,

	TRIS +	HCl $\rightleftharpoons$	TRISH$^+$ + Cl$^-$
In	x	0.095	0.00
△	-0.095	-0.095	+0.095
End	x-0.095	0.00	0.095

$$\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = \frac{x - 0.095}{0.095} = 2.75$$

Solve for x (mol TRIS added)

x = 0.356 mol TRIS x 121.14 g/mol = 43.1 g TRIS