

## Chapter 17: Additional Aspects of Aqueous Equilibria

### Kahoot!

- Adding Br<sup>-</sup> to a saturated aqueous solution of \_\_\_\_ decreases its solubility in water. BaSO<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, PbS, AgBr
- Which of the following mixtures could be used to prepare an effective buffer? HCl and KCl, HNO<sub>3</sub> and KNO<sub>3</sub>, HCl and NH<sub>4</sub>Cl, NH<sub>3</sub> and NH<sub>4</sub>Cl
- Which 1 L solution has the greatest buffer capacity? 0.1 M NH<sub>3</sub> and 0.1 M NH<sub>4</sub>Cl, 0.05 M NH<sub>3</sub> and 0.05 M NH<sub>4</sub>Cl, 0.1 M NH<sub>3</sub> and 0.01 M NH<sub>4</sub>Cl, 0.5 M NH<sub>3</sub> and 0.5 M NH<sub>4</sub>Cl
- Select the best acid or base to pair with its conjugate salt to prepare a 8.5 pH buffer. acetic acid; K<sub>a</sub> = 1.8x10<sup>-5</sup>, ammonia; K<sub>b</sub> = 1.8x10<sup>-5</sup>, hydroxylamine; K<sub>b</sub> = 1.1x10<sup>-8</sup>, citric acid; K<sub>a</sub> = 7.5x10<sup>-4</sup>
- Select the correct representation of the Henderson-Hasselbalch equation. K<sub>a</sub> = [H<sup>+</sup>][A<sup>-</sup>], K<sub>w</sub> = [H<sup>+</sup>][OH<sup>-</sup>] = 10<sup>-14</sup>, pH = pK<sub>a</sub> + log [base]/[acid], pK<sub>a</sub> = pH + log[base]/[acid]
- Which indicator is preferable when titrating a weak base with a strong acid? Methyl red (color change pH = 5), bromothymol blue (pH = 7), phenolphthalein (pH = 9), None of the above
- Which indicator is preferable when titrating a weak acid with a strong base? Methyl red (color change pH = 5), bromothymol blue (pH = 7), phenolphthalein (pH = 9), None of the above
- For BaCO<sub>3</sub>, K<sub>sp</sub> = 5.0 x 10<sup>-9</sup>. What is [Ba<sup>2+</sup>]? 7.1 x 10<sup>-5</sup> M, 1.0 x 10<sup>-8</sup> M, 2.5 x 10<sup>-9</sup> M, 5.0 x 10<sup>-9</sup> M
- For BaF<sub>2</sub>, K<sub>sp</sub> = 1.7 x 10<sup>-6</sup>. What is [Ba<sup>2+</sup>]? 1.7 x 10<sup>-6</sup> M, 3.4 x 10<sup>-6</sup> M, 7.6 x 10<sup>-3</sup> M, 1.5 x 10<sup>-2</sup> M
- Which of the following reagents will reduce the solubility of BaF<sub>2</sub>? NaCl, Ba(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>, KOH, NH<sub>4</sub>Br
- Which of the following reagents will increase the solubility of BaF<sub>2</sub>? HCl, HF, KOH, NH<sub>4</sub>Br

### Whiteboard Examples

**Example:** Calculate the pH of a solution prepared by mixing equal volumes of 0.20 M CH<sub>3</sub>NH<sub>2</sub> and 0.60 M CH<sub>3</sub>NH<sub>3</sub>Cl (K<sub>b</sub> = 3.7 x 10<sup>-4</sup>). What is the pH of 0.20 M CH<sub>3</sub>NH<sub>2</sub> without addition of CH<sub>3</sub>NH<sub>3</sub>Cl? assuming we have 1 L of each

$$[\text{CH}_3\text{NH}_2]_0 = \frac{0.20 \text{ moles CH}_3\text{NH}_2 \times 1 \text{ L}}{2.0 \text{ L}} = 0.10 \text{ M CH}_3\text{NH}_2$$

$$[\text{CH}_3\text{NH}_3^+]_0 = \frac{0.60 \text{ moles CH}_3\text{NH}_3^+ \times 1 \text{ L}}{2.0 \text{ L}} = 0.30 \text{ M CH}_3\text{NH}_3^+$$

I	0.1	-	0.3	0
C	-x	-	+x	+x
E	0.1 - x	-	0.3 + x	+x

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(0.3+x)x}{0.1-x} = 3.7 \times 10^{-4}$$

$$x^2 + 0.3004x - 3.7 \times 10^{-5} = 0$$

$$x = 8.97 \times 10^{-5} \text{ M OH}^-$$

$$\text{pH} = 14 + \log(8.97 \times 10^{-5}) = 9.95$$

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pH of 0.20 M CH<sub>3</sub>NH<sub>2</sub>:

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{x^2}{0.1-x} = 3.7 \times 10^{-4}$$

$$x^2 + 3.7 \times 10^{-4}x - 3.7 \times 10^{-5} = 0$$

$$x = 8.24 \times 10^{-3} \text{ M } OH^-$$

$$pH = 14 + \log(8.24 \times 10^{-3}) = 11.92$$

**Buffer Example I:** Calculate the pH and pOH of a 500.0mL solution containing

0.225M  $HPO_4^{2-}$  and 0.225M  $PO_4^{3-}$  at 25°C where the  $K_a(HPO_4^{2-}) = 4.2 \times 10^{-13}$ .

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = -\log(4.2 \times 10^{-13}) + \log\left(\frac{0.225M}{0.225M}\right)$$

$$pH = 12.38$$

**Buffer Example II:** How would we prepare a pH = 4.44 buffer using  $CH_3CO_2H$  and  $CH_3CO_2Na$ ?

$$K_a = 1.8 \times 10^{-5}$$

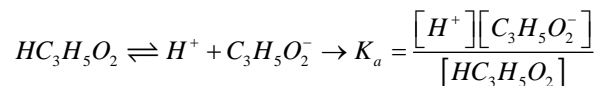
$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \rightarrow \log\left(\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}\right) = 4.44 + \log(1.8 \times 10^{-5}) = -0.305$$

$$\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = 10^{-0.305} = 0.496$$

Therefore, in order to make a 4.44 buffer solution we need 0.496 moles of  $CH_3CO_2Na$  for every mole of  $CH_3CO_2H$

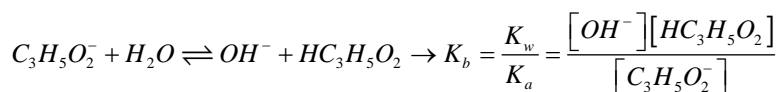
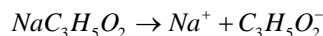
**Comprehensive Example:** Calculate the pH of each of the following solutions:

a. 0.100 M  $HC_3H_5O_2$ ,  $K_a = 1.3 \times 10^{-5}$



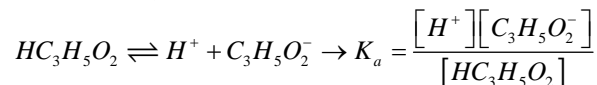
$$1.3 \times 10^{-5} = \frac{x^2}{0.100 - x} \rightarrow x = 1.1 \times 10^{-3} \text{ M } H^+ \quad pH = 2.96$$

b. 0.100 M  $NaC_3H_5O_2$



$$7.7 \times 10^{-10} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \rightarrow x = 8.8 \times 10^{-6} \text{ M } OH^- \quad pH = 14 - pOH = 8.94$$

c. a mixture containing a. & b.



$$1.3 \times 10^{-5} = \frac{(0.100 + x)x}{0.100 - x} \rightarrow x = 1.3 \times 10^{-5} \text{ M } H^+ \quad pH = 4.89$$

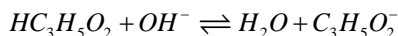
$$\text{using Henderson-Hasselbach, } pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = -\log 1.3 \times 10^{-5} + \log\left(\frac{0.100}{0.100}\right) = 4.89$$

d. a mixture containing c. and 0.020 mol of NaOH

when strong base is added to an acid containing solution it will

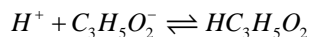
neutralize the acid and so all of the  $\text{OH}^-$  will react completely with our propanoic acid



	$\text{HC}_3\text{H}_5\text{O}_2$	$\text{OH}^-$	$\text{C}_3\text{H}_5\text{O}_2^-$
B	0.100	0.020	0.100
C	-0.020	-0.020	+0.02
A	0.080	0	0.120

$$\text{pH} = -\log 1.3 \times 10^{-5} + \log \left( \frac{0.120}{0.080} \right) = 5.06$$

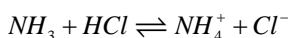
e. a mixture containing c. and 0.020 mol of HCl



	$\text{C}_3\text{H}_5\text{O}_2^-$	$\text{H}^+$	$\text{HC}_3\text{H}_5\text{O}_2$
B	0.100	0.020	0.100
C	-0.020	-0.020	+0.02
A	0.080	0	0.120

$$\text{pH} = -\log 1.3 \times 10^{-5} + \log \left( \frac{0.080}{0.120} \right) = 4.71$$

**Titration Example I:** What is  $[\text{NH}_3]$  if 22.35 mL of 0.1145 M HCl were needed to titrate a 100.0 mL sample?



$$[\text{NH}_3] = 0.02235 \text{ L} \times \frac{0.1145 \text{ moles HCl}}{\text{L}} \times \frac{1 \text{ mole NH}_3}{1 \text{ mole HCl}} \times \frac{1}{0.1000 \text{ L}} = 0.02259 \text{ M}$$

**Titration Example II – Strong with Strong:** A 15.0 mL sample of 0.200 M NaOH is titrated with 0.250 M of HCl. Calculate the pH of the mixture after 10.0, and 20.0 mL of acid have been added.

If you are not given a dissociation constant this should remind you that the acid/base is strong.

For 10.0 mL of HCl & 15.0 mL of NaOH:

$$10.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol H}^+_{(aq)}}{1 \text{ L}} = 0.00250 \text{ mol H}^+_{(aq)}$$

$$15.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.200 \text{ mol OH}^-_{(aq)}}{1 \text{ L}} = 0.00300 \text{ mol OH}^-_{(aq)}$$

	$\text{H}^+_{(aq)}$	$\text{OH}^-_{(aq)}$	$\text{H}_2\text{O}_{(l)}$
B	0.00250	0.00300	-
C	-0.00250	-0.00250	-
A	0	0.00050	-

$$[\text{OH}^-] = \frac{0.0005 \text{ moles}}{0.025 \text{ L}} = 0.0200 \text{ M}$$

$$\text{pH} = 14 + \log(0.02) = 12.30$$

For 20.0 mL of HCl

$$20.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol H}^+_{(aq)}}{1 \text{ L}} = 0.00500 \text{ mol H}^+_{(aq)}$$

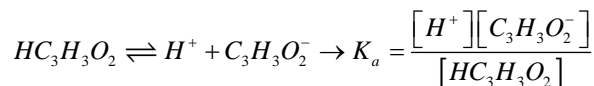
	$\text{H}^+_{(aq)}$	$\text{OH}^-_{(aq)}$	$\text{H}_2\text{O}_{(l)}$
B	0.00500	0.00300	-
C	-0.00300	-0.00300	-
A	0.00200	0	-

$$[H^+] = \frac{0.002 \text{ moles}}{0.035L} = 0.05714M$$

$$pH = -\log(0.05714) = 1.24$$

**Titration Example III – Strong with Weak:** A 25.0 mL sample of 0.100 M acetic acid ( $HC_2H_3O_2$ ) is titrated with 0.125 M of NaOH. Calculate the pH of the mixture after 0.0, 10.0, 20.0, and 30.0 mL of base have been added. ( $K_a = 1.8 \times 10^{-5}$ )

For 0.0 mL it is the same as a weak acid:



$$1.8 \times 10^{-5} = \frac{x^2}{0.100 - x}$$

assume  $x \ll 0.100$

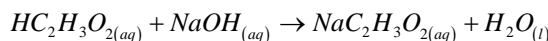
$$1.8 \times 10^{-5} \sim \frac{x^2}{0.100} \rightarrow x = 1.34 \times 10^{-3} M H^+$$

$$\text{verify assumption: } \frac{1.34 \times 10^{-3}}{0.100} \times 100\% = 1.34\% < 5\%$$

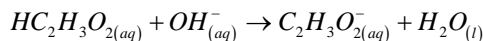
$$pH = -\log(1.1 \times 10^{-3}) = \boxed{2.87}$$

For 10.0 mL:

Initially we have:



$Na^+$  is a spectator ion so we are really looking at:

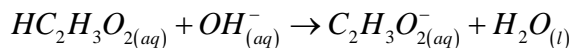


This is in fact a neutralization reaction. For 10.0 mL of NaOH:

$$25.0 \text{ mL} \times \frac{1 L}{1000 \text{ mL}} \times \frac{0.100 \text{ mol } HC_2H_3O_2(aq)}{1 L} = 0.00250 \text{ mol } HC_2H_3O_2(aq)$$

$$10.0 \text{ mL} \times \frac{1 L}{1000 \text{ mL}} \times \frac{0.125 \text{ mol } OH^-(aq)}{1 L} = 0.00125 \text{ mol } OH^-(aq)$$

Now we set up a "BCA" table or before, change, after table



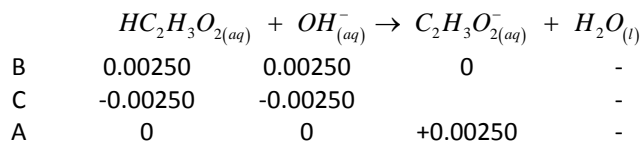
B	0.00250	0.00125	0	-
C	-0.00125	-0.00125		-
A	0.00125	0	+0.00125	-

So, we have neutralized the acid with the given amount of base and are now ready to apply the Henderson-Hasselbalch equation:

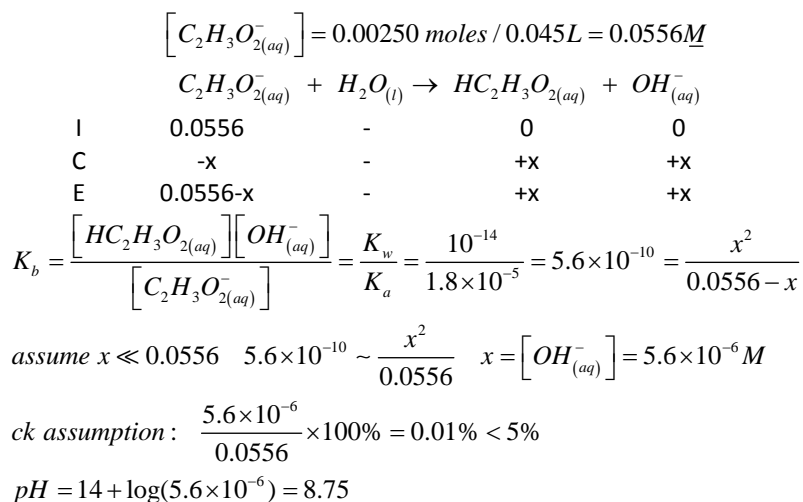
$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.0125}{\frac{0.0350L}{0.0125}}\right) = 4.74$$

Time for 20.0 mL of NaOH:

$$20.0 \text{ mL} \times \frac{1 L}{1000 \text{ mL}} \times \frac{0.125 \text{ mol } OH^-(aq)}{1 L} = 0.00250 \text{ mol } OH^-(aq)$$



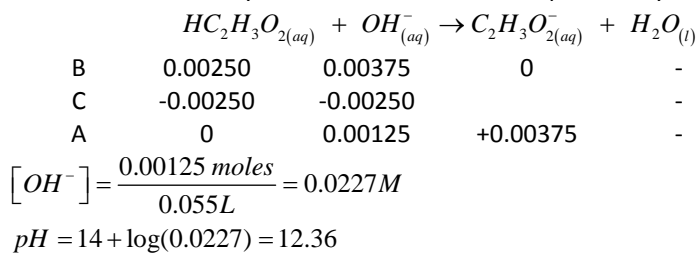
All of the acid has reacted with all the base and so we are now at the equivalence point. However, since we had a weak acid and a strong base we should expect our pH to be higher than 7. To find the pH we need an "ICE" table.



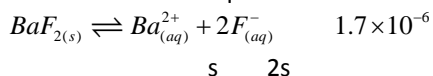
Finally, 30.0 mL

$$30.0 \text{ mL} \times \frac{1 L}{1000 \text{ mL}} \times \frac{0.125 \text{ mol } OH^-(aq)}{1 L} = 0.00375 \text{ mol } OH^-(aq)$$

Now, we have more strong base than acid so we can set up the BCA table and then determine hydroxide concentration and pH directly.



**Solubility Example:** Determine the equilibrium concentrations (and solubilities) of  $BaF_2(s)$ ,  $K_{sp} = 1.7 \times 10^{-6}$ .



$$K_{sp} = [S][2S]^2$$

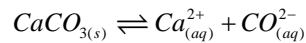
$$1.7 \times 10^{-6} = 4S^3 \rightarrow S = 0.0075M$$

$$[Ba^{2+}] = 0.0075M \quad \text{and} \quad [F^-] = 2 \times 0.0075 = 0.015M$$

$$Ba^{2+} : \frac{0.0075 \text{ moles}}{L} \times \frac{137.327 \text{ g}}{\text{mol}} = 1.03 \frac{\text{g}}{L}$$

$$F^- : \frac{0.015 \text{ moles}}{L} \times \frac{18.998 \text{ g}}{\text{mol}} = 0.285 \frac{\text{g}}{L}$$

**Common-Ion Solubility Example:** Calculate the solubility of calcite ( $CaCO_3$ ) in 0.00100 M of  $Na_2CO_3$  and in just plain water ( $K_{sp} = 4.5 \times 10^{-9}$  at 25°C).



	$\text{Ca}_{(aq)}^{2+}$	$\text{CO}_{(aq)}^{2-}$
Initial	0	0.0010
Change	+s	+s
Eq	s	0.0010+s

$$K_{sp} = [s][0.001 + s]$$

assume  $0.001 \gg s$

$$K_{sp} = 4.5 \times 10^{-9} \sim 0.001s \rightarrow s = 4.5 \times 10^{-6} M$$

$$ck: \frac{4.5 \times 10^{-6}}{0.001} \times 100\% = 0.45\% < 5\%$$

Therefore the solubility of  $\text{CaCO}_3$  is  $4.5 \times 10^{-6} M$  with  $[\text{Ca}^{2+}] = 4.5 \times 10^{-6} M$  &  $[\text{CO}_3^{2-}] = 0.0010 M$   
How does this compare with the solubility of just  $\text{CaCO}_3$ ?

	$\text{Ca}_{(aq)}^{2+}$	$\text{CO}_{(aq)}^{2-}$
Initial	0	0.0010
Change	+s	+s
Eq	s	+s

$$K_{sp} = [s][s]$$

$$4.5 \times 10^{-9} = s^2 \rightarrow s = 6.71 \times 10^{-5} M$$

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = 6.71 \times 10^{-5} M$$

$6.71 \times 10^{-5} M > 4.5 \times 10^{-6} M$  thereby demonstrating how common-ion represses solubility