

Chapter 17 – Additional Aspects of Aqueous Equilibria

• 17.1 The Common Ion Effect

- common ions: when two different solutes give rise to the same ion (cation/anion)
 - e.g. NaCl and HCl both give rise to Cl^-
 - by having two sources of the same ion we will repress the dissociation of the acid or base under examination
- common ion effect: a shift in equilibrium due to the addition of a common ion
 - based on Le Châtelier's Principle
 - example: $\text{H}_2\text{CO}_{3(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq)$
 - if we add $\text{HCO}_3^-(aq)$ then the eq shifts to the left
 - therefore we will not produce as much $\text{H}_3\text{O}^+(aq)$
 - we will have a higher pH than we would have had
 - example: Calculate the pH of a solution prepared by mixing equal volumes of 0.20 M CH_3NH_2 and 0.60 M $\text{CH}_3\text{NH}_3\text{Cl}$ ($K_b = 3.7 \times 10^{-4}$). What is the pH of 0.20 M CH_3NH_2 without addition of $\text{CH}_3\text{NH}_3\text{Cl}$? assuming we have 1 L of each

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

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

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

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

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

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

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

pH of 0.20 M CH_3NH_2 :

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{x^2}{0.1-x} = 3.7 \times 10^{-4}$$

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

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

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

• 17.2 Buffers

- pH buffer: a solution that resists changes in pH
 - they are made with solutions which have either a base and its conj acid or with an acid and its conj base

- therefore the result of the common-ion effect
- buffer capacity: the quantity of acid/base needed to significantly change the pH of a buffer
 - the larger the buffer capacity the larger this amount is
 - depends upon the number of moles of acid/base are present in solution
 - for equal volumes - the more concentrated the solutions the larger the buffer capacity
 - for equal moles of acid/base - the larger the volume the larger the buffer capacity
- Henderson-Hasselbalch – MEMORIZE!
 - we use this equation when we need to make or have a buffer
 - Ex: 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 $K_a(HPO_4^{2-}) = 4.2 \times 10^{-13}$.

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

$$pH = 12.38$$

- Ex: How would we prepare a pH = 4.44 buffer using CH_3CO_2H and CH_3CO_2Na ? $K_a = 1.8 \times 10^{-5}$

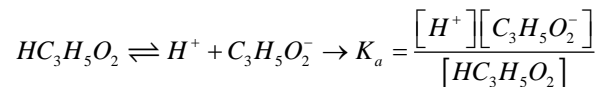
$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \rightarrow \log\left(\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}\right) = 4.44 + \log(1.8 \times 10^{-5}) = -0.305$$

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

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

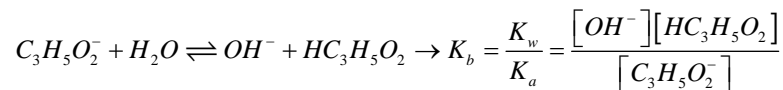
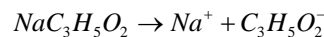
- Here are a set of examples which show how pH is impacted starting with a weak acid, then looking at a salt solution with the weak acid's conjugate base, then we put the two together forming a buffer and finally we see the effect of adding a small amount of acid and base to a buffer

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



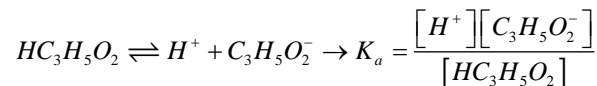
$$1.3 \times 10^{-5} = \frac{x^2}{0.100 - x} \rightarrow x = 1.1 \times 10^{-3} M H^+ \quad pH = 2.96$$

- b. 0.100 M $NaC_3H_5O_2$



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

- c. a mixture containing a. & b.



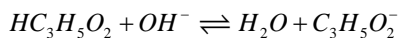
$$1.3 \times 10^{-5} = \frac{(0.100 + x)x}{0.100 - x} \rightarrow x = 1.3 \times 10^{-5} M H^+ \quad pH = 4.89$$

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

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

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

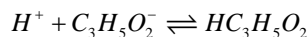
when strong base is added to an acid containing solution it will neutralize the acid and so all of the OH^- will react completely with our propanoic acid



	$\text{HC}_3\text{H}_5\text{O}_2$	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

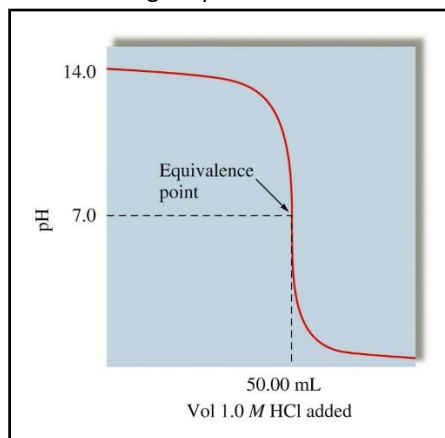


	$\text{C}_3\text{H}_5\text{O}_2^-$	H^+	$\text{HC}_3\text{H}_5\text{O}_2$
B	0.100	0.020	0.100
C	-0.020	-0.020	+0.02
A	0.080	0	0.120

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

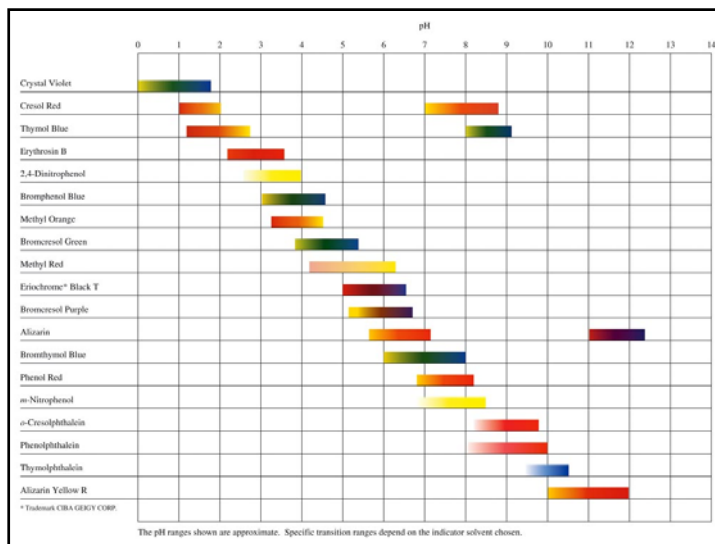
• 17.3 Acid-Base Titrations

- we do titrations to determine conc'ns of species
- we continue to add titrant until we have exactly the correct number of moles of titrant to neutralize that of the analyte we are measuring
 - when this occurs we have reached the endpoint or equivalence point
- pH versus volume – the titration curve
 - when a single endpt occurs there is only one species interacting with the titrant e.g. $\text{HCl} + \text{NaOH}$
 - when more than one species is reacting with the titrant we will have two endpts e.g. $\text{K}^+ + \text{Fe}^{3+} + \text{NaOH}$
 - if acid is the titrant, we start out at a higher pH



--- if we use a strong acid with a strong base, our endpt occurs at $\text{pH} = 7$

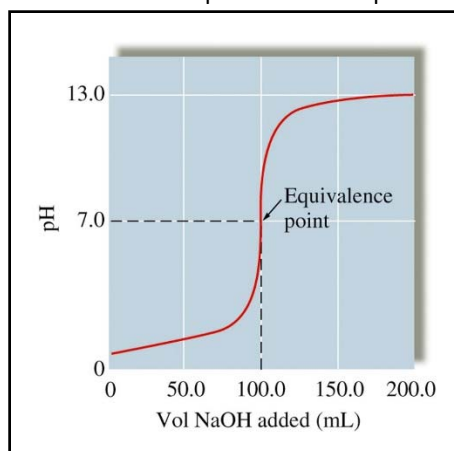
---- for this situation we want an indicator that has a color change of around $\text{pH} 7$ which according to our indicator chart see



--- if we use a strong acid with a weak base, our endpt occurs at pH < 7

---- indicators, range from crystal violet to bromothymol blue

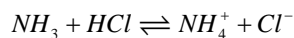
-- if base is the titrant, we start out at a lower pH and our endpt occurs at a higher pH



--- if we use a strong base with a weak acid, our endpt occurs at a pH > 7

---- indicators, range from phenol red to alizarin yellow R and possibly thymol blue

- Ex: What is $[NH_3]$ if 22.35mL of 0.1145 M HCl were needed to titrate a 100.0mL sample?



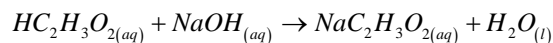
$$[NH_3] = 0.02235L \times \frac{0.1145 \text{ moles HCl}}{L} \times \frac{1 \text{ mole } NH_3}{1 \text{ mole HCl}} \times \frac{1}{0.1000L} = 0.02259M$$

- Titration Examples:

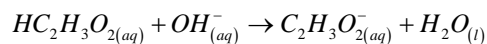
-- *The Strong & The Weak:*

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 10.0, 20.0, and 30.0 mL of base have been added. ($K_a = 1.8 \times 10^{-5}$)

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:

$$25.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.100 \text{ mol } HC_2H_3O_{2(aq)}}{1 \text{ L}} = 0.00250 \text{ mol } HC_2H_3O_{2(aq)}$$

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

Now we set up a "BCA" table or before, change, after table (it is in mol not mol/L hence the difference)

	$HC_2H_3O_{2(aq)}$	$+ OH_{(aq)}^-$	$\rightarrow C_2H_3O_{2(aq)}^-$	$+ H_2O_{(l)}$	
B	0.00250	0.00125	0		-
C	-0.00125	-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:

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

	$HC_2H_3O_{2(aq)}$	$+ OH_{(aq)}^-$	$\rightarrow C_2H_3O_{2(aq)}^-$	$+ H_2O_{(l)}$	
B	0.00250	0.00250	0		-
C	-0.00250	-0.00250	+0.00250		-
A	0	0	+0.00250		-

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.

$$[C_2H_3O_{2(aq)}^-] = 0.00250 \text{ moles} / 0.045L = 0.0556M$$

	$C_2H_3O_{2(aq)}^-$	$+ H_2O_{(l)}$	$\rightarrow HC_2H_3O_{2(aq)}$	$+ OH_{(aq)}^-$	
I	0.0556	-	0	0	
C	-x	-	+x	+x	
E	0.0556-x	-	+x	+x	

$$K_b = \frac{[HC_2H_3O_2(aq)][OH_{(aq)}^-]}{[C_2H_3O_2^-(aq)]} = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{x^2}{0.0556 - x}$$

assume $x \ll 0.0556$ $5.6 \times 10^{-10} \sim \frac{x^2}{0.0556}$ $x = [OH_{(aq)}^-] = 5.6 \times 10^{-6} M$

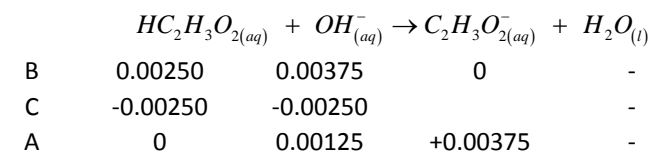
ck assumption: $\frac{5.6 \times 10^{-6}}{0.0556} \times 100\% = 0.01\% < 5\%$

$pH = 14 + \log(5.6 \times 10^{-6}) = 8.75$

Finally, 30.0 mL

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

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



$$[OH^-] = \frac{0.00125 \text{ moles}}{0.055 \text{ L}} = 0.0227 M$$

$pH = 14 + \log(0.0227) = 12.36$

- The Strong & the Strong: HCl & NaOH

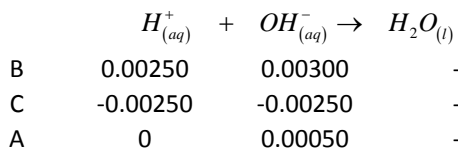
A 15.0 mL sample of 0.200 M NaOH is titrated with 0.250 M of HCl. Calculate the pH of the mixture after 10.0, and 20.0 mL of acid have been added.

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:

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

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

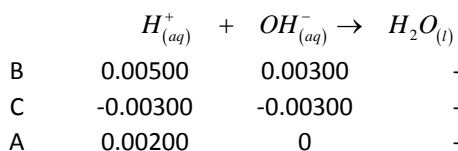


$$[OH^-] = \frac{0.0005 \text{ moles}}{0.025 \text{ L}} = 0.0200 M$$

$pH = 14 + \log(0.02) = 12.30$

For 20.0 mL of HCl

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



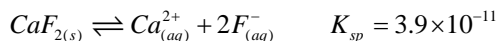
$$[H^+] = \frac{0.002 \text{ moles}}{0.035L} = 0.05714M$$

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

- Titrations of Polyprotic Acids – SKIP!

• 17.4 Solubility Equilibria

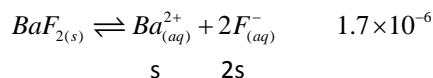
- K_{sp} is called the solubility product and is the eq constant for solids in solution



$$K_{sp} = [Ca_{(aq)}^{2+}][F_{(aq)}^-]^2$$

- In general, $M_m X_x \rightleftharpoons mM_{(aq)} + xX_{(aq)} \quad K_{sp} = [M]^m [X]^x$

- Ex: Determine the equilibrium concentrations (and solubilities) of $BaF_{2(s)}$, $K_{sp} = 1.7 \times 10^{-6}$.



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

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

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

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

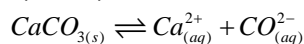
$$F^- : \frac{0.015 \text{ moles}}{L} \times \frac{18.998 \text{ g}}{\text{mol}} = 0.285 \frac{\text{g}}{L}$$

• 17.5 Factors that Affect Solubility

- common ion effect -- just like it affects the pH it will affect our solubility

-- to deal with this problem we must once again invoke the ICE table

-- Ex: Calculate the solubility of calcite ($CaCO_3$) in 0.00100 M of Na_2CO_3 ($K_{sp} = 4.5 \times 10^{-9}$ at $25^\circ C$).



	$Ca_{(aq)}^{2+}$	$CO_{(aq)}^{2-}$
Initial	0	0.0010
Change	+s	+s
Eq	s	0.0010+s

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

assume $0.001 \gg s$

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

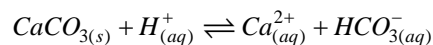
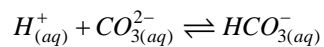
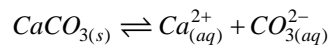
$$ck : \frac{4.5 \times 10^{-6}}{0.001} \times 100\% = 0.45\% < 5\%$$

Therefore the solubility of $CaCO_3$ is $4.5 \times 10^{-6} M$

- pH of solution

-- if a salt contains the conjugate base of a weak acid then it will be affected by the pH

-- ex: $CaCO_3$ in acidic solution



--- when CaCO_3 comes into contact with acidic solution it will dissolve

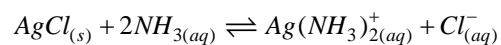
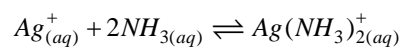
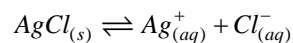
-- This will not be a factor for the conjugate bases of strong acids since they will not reform their acidic counterparts

- formation of complex ions

-- if a ligand is added to a solution containing the salt it could lead to complex ion formation

-- if this occurs then the amount of metallic cation is reduced therefore pushing eq to the right, causing the salt to become more soluble

-- ex: AgCl and NH_3



- Amphoterism – SKIP!

• **17.6 Precipitation & Separation of Ions & 17.7 Qualitative Analysis for Metallic Elements – Skip!**