These Notes are to <u>SUPPLIMENT</u> the Text, They do NOT Replace reading the Text Book Material. Additional material that is in the Text Book will be on your tests! To get the most information, <u>READ THE CHAPTER</u> prior to the Lecture, bring in <u>these lecture notes and make comments on these notes.</u> <u>These notes alone are NOT enough to pass any test!</u>
<u>NOTE THESE ARE DRAFT LECTURE NOTES!</u>

18.1 Common Ion Effect
What happens to the pH of Acetic Acid when it's conjugate base, Acetate, is added?

Common Ion Effect: change produce by adding additional conjugate acid/base to a acid/base solution. E.g. Add Sodium Acetate (CH_3-COO^- Na^+) to Acetic Acid (CH_3-$COOH$).

1.0 L of 0.25 M Acetic Acid has a pH of 2.67 (prove it), what happens when 0.10 mol of Sodium Acetate is added? $Ka = [H^+][CH_3$-$COO^-] = 1.8 \times 10^{-5}$

<u>Prove pH of Acetic Acid:</u>   (Note: This is not in the book)

	CH_3-$COOH$ ⇋	H^+	CH_3-COO^-
Initial	0.25	0	0
Change	-x	+x	+x
Equilibrium	0.25-x	x	x

$Ka = $ x * x / (0.25 - **x**) $= 1.8 \times 10^{-5}$ **Assume** (0.25 - **x**) = 0.25

$x^2 / 0.25 = 1.8 \times 10^{-5}$ $x = (0.25 * 1.8 \times 10^{-5})^{1/2} = 2.12 \times 10^{-3} = [H^+]$

Prove Assumption: $(0.25) = (0.25 - $ **x**$) = (0.25 - 2.12 \times 10^{-3}) = $ **Assumption is True**

$pH = -\log([H^+]) = -\log(2.12 \times 10^{-3}) = $ **2.67**

<u>Solve Problem:</u>

	CH_3-$COOH$ + HOH ⇋	H_3O^+ +	CH_3-COO^-
Initial	0.25	0	0.10
Change	-x	+x	+x
Equilibrium	0.25 - x	x	x + 0.10

$Ka = 1.8 \times 10^{-5} = [H_3O^+][CH_3$-$COO^-] / [CH_3$-$COOH] = $ x * (**x** + 0.10) / (0.25 - **x**)

Again, Ka is small so x is small, **Assume** (**x** + 0.10) = (0.10) and (0.25 - **x**) = (0.25)

$1.8 \times 10^{-5} = $ x * 0.10 / 0.25 $x = 1.8 \times 10^{-5} * 0.25 / 0.10 = $ **$4.5 \times 10^{-5} = [H_3O^+]$**

Prove Assumption: $(0.10) = (x + 0.10) = (4.5 \times 10^{-5} + 0.10) = $ **Assumption is True**

$pH = -\log([H_3O^+]) = -\log(4.5 \times 10^{-5}) = $ **4.35**

Per Le Chatelier's Principal, take Acetic Acid at a pH of 2.67, add some Acetate, ion on the right of the balanced equation above, the equilibrium is shifted to the left, uses up some acid, so pH goes more basic to 4.35!

Interactive Example 18.1   ? is pH of solution of 25.0 ml of 0.0500 M NaOH added to 25.0 ml

of 0.100 M Lactic Acid (CH_3-$CHOH$-$COOH$). Ka for Lactic Acid is 1.4×10^{-4}

Hint: All of the NaOH (a strong base) will be used up

Calculate the moles of each: # Moles = Molarity * Volume

    NaOH   # Moles = 0.0500 M * 25.0 ml * 1 L / 1000 ml = 1.25×10^{-3} Moles

    Lactic acid   # Moles = 0.100 M 25.0 ml * 1 L / 1000 ml   = 2.50×10^{-3} Moles

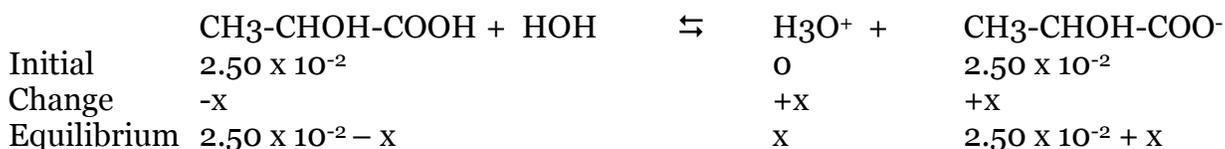Lactic acid to NaOH **reaction ratio** is 1/1, so Lactic acid is in excess, NaOH is Limiting Reagent

Lactic acid remaining = 2.50×10^{-3} Moles, Lactic Acid - 1.25×10^{-3} Moles NaOH = 1.25×10^{-3} Moles

And the amount of Lactic Ion formed = the amount of NaOH = 1.25×10^{-3} Moles

Note: Book makes above more complicated than it really is!

Lactic Acid Concentration is 1.25×10^{-3} Moles * 1000 ml / (25.0 ml + 25.0 ml) * 1 L = 2.50×10^{-2} M

Lactic Ion Concentration is 1.25×10^{-3} Moles * 1000 ml / (25.0 ml + 25.0 ml) * 1 L = 2.50×10^{-2} M

	$CH_3\text{-}CHOH\text{-}COOH$ + HOH	⇌	H_3O^+ +	$CH_3\text{-}CHOH\text{-}COO^-$
Initial	2.50×10^{-2}		0	2.50×10^{-2}
Change	-x		+x	+x
Equilibrium	$2.50 \times 10^{-2} - x$		x	$2.50 \times 10^{-2} + x$

$Ka = 1.4 \times 10^{-4}$ $= [H_3O^+][CH_3\text{-}CHOH\text{-}COO^-] / [CH_3\text{-}CHOH\text{-}COOH]$

                 $= x * (2.50 \times 10^{-2} + \underline{x}) / (2.50 \times 10^{-2} - \underline{x})$

Assume x is small then $(2.50 \times 10^{-2} + \underline{x}) = 2.50 \times 10^{-2}$ and $(2.50 \times 10^{-2} - \underline{x}) = 2.50 \times 10^{-2}$

    $1.4 \times 10^{-4} =$ $x * 2.50 \times 10^{-2} / 2.50 \times 10^{-2}$ or $\mathbf{x = 1.4 \times 10^{-4} = H_3O^+}$

    Prove Assumption $(2.50 \times 10^{-2} + x) = (0.0250 - 00014) =$ **Close enough to be true**

    pH = - log (H_3O^+) = - log $(1.4 \times 10^{-4}) =$ **3.85**

18.2 Controlling pH: Buffer Solutions
A Buffer Solution is a solution that resists a change in pH when acid or base is added

    Add 0.010 mol of HCl to 1.0 L of pure water, the pH drops from 7 to 2

    Add 0.010 mol of NaOH to pure water, the pH increases from 7 to 12

Buffer Requirements:
    2 compounds are needed   an acid capable of reacting with OH^-
                                    a base that can react with H_3O^+

    The acid and base must not react with each other

A Conjugate acid-base pair will work
    A weak acid and its conjugate base   Acetic Acid CH_3COOH and Acetate CH_3COO^-
    A weak base and it's conjugate acid   Ammonia NH_3 an Ammonium Ion NH_4^+
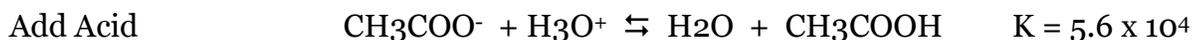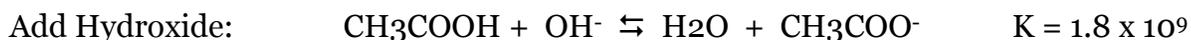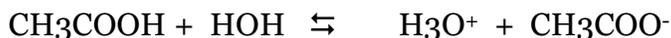
How the Acetic Acid / Acetate buffer works:

                      CH_3COOH + HOH ⇌ H_3O^+ + CH_3COO^-

    Add Hydroxide: CH_3COOH + OH^- ⇌ H_2O + CH_3COO^- $K = 1.8 \times 10^9$

    Add Acid CH_3COO^- + H_3O^+ ⇌ H_2O + CH_3COOH $K = 5.6 \times 10^4$

Table 18.1 Some Commonly Used Buffer Systems

Weak Acid	Conjugate Base	Acid K_a (pK_a)	Useful pH Range
Phthalic acid, $C_6H_4(CO_2H)_2$	Hydrogen phthalate ion, $C_6H_4(CO_2H)(CO_2)^-$	1.3×10^{-3} (2.89)	1.9–3.9
Acetic acid, CH_3CO_2H	Acetate ion, $CH_3CO_2^-$	1.8×10^{-5} (4.74)	3.7–5.8
Dihydrogen phosphate ion, $H_2PO_4^-$	Hydrogen phosphate ion, HPO_4^{2-}	6.2×10^{-8} (7.21)	6.2–8.2
Hydrogen phosphate ion, HPO_4^{2-}	Phosphate ion, PO_4^{3-}	3.6×10^{-13} (12.44)	11.4–13.4

Interactive Example 18.2   ? pH of a solution 0.700 M Acetic Acid, 0.600 M Sodium Acetate

	CH_3COOH + HOH $\leftrightarrows$	H_3O^+ +	CH_3COO^-
Initial	0.700	0	0.600
Change	-x	+x	+x
Equilibrium	0.700 – x	x	0.600 + x

$Ka = 1.8 \times 10^{-5} = [H_3O^+][CH_3COO^-] / [CH_3COOH] = x (0.600 + \underline{x}) / (0.700 - \underline{x})$

Assume x is small (run test), so $(0.600 + \underline{x}) = 0.600$ and $(0.700 - \underline{x}) = 0.700$

$1.8 \times 10^{-5} = x * 0.600 / 0.700$ $x = 1.8 \times 10^{-5} * 0.700 / 0.600 =$ **$2.1 \times 10^{-5} = [H_3O^+]$**

Prove Assumption $(0.600 + x) = (0.500 + 2.1 \times 10^{-5}) = 0.500$ **Assumption is True**

$pH = - \log([H_3O^+]) = - \log(2.1 \times 10^{-5}) =$ **4.68**

General Formulae: **$[H_3O^+] = Ka * [acid] / [conjugate base]$**

<u>Henderson-Hasselbalch Equation:</u>   **$pH = pKa + \log([conjugate base] / [acid])$**

The pH of a buffer is determined by:

    The strength of the acid expressed as Ka or pKa

    The relative amount of acid and conjugate base

Note: When the concentration of [conjugate base] = [acid] then: pH = pKa + log (1) = pKa + 0

    If **[conjugate base] > [acid],** then pH = pKa + log (2) = pKa + 0.3 or   **pH > pKa**

    If **[conjugate base] < [acid],** then pH = pKa + log (.2) = pKa - 0.7 or   **pH < pKa**

Interactive Example 18.3
2.00 g Benzoic Acid (C_6H_5COOH, mw 122.1 g/mol) and 2.00 g Sodium Benzoate ($C_6H_5COO^-$ Na^+, mw 144.1 g/mol) mixed with water to make 1.00 L. Ka Benzoic Acid = 6.3×10^{-5}.   ? pH

Calculate the molar concentration of each:

    Benzoic Acid   2.00 g / 122.1 g /mol = 0.0164 mol   0.0164 mol / 1 L = 0.0164 M

    Sodium Benzoate   2.00 g / 144.1 g/mol = 0.0139 mol   0.0139 mol / 1 L = 0.0139 M

    pKa Benzoic Acid = - log (Ka) = - log (.3 x 10-5) = 4.20

    pH = pKa + log ([conjugate base] / [acid]) = 4.20 + log (0.0139 / 0.0163) = **4.13**

Preparing Buffer Solutions
Example 18.4 Preparing a Buffer Solution How would you prepare 1.0 L of a pH 4.30 buffer

Acid	Conjugate Base	Ka
HSO_4^-	SO_4^{2-}	1.2×10^{-2}
CH_3COOH	CH_3COO^-	1.8×10^{-5}
HCO_3^-	CO_3^{2-}	4.8×10^{-11}

Easy Solution: CH_3COOH with a Ka of 1.8×10^{-5}, the -5 says the pH will be less than 5 or in the 4's
This is the buffer to use.

HSO_4^- with a Ka of 1.2×10^{-2} will have a pH of less then 2, that no good

HCO_3^- with a Ka of 4.8×10^{-11} will have a pH of less than 11, that's no good!

$[H_3O^+]$ = Ka * [acid] / [conjugate base]

[acid] / [conjugate base] = $[H_3O^+]$ / Ka = $10^{-4.13}$ / 1.8×10^{-5} = 5.0×10^{-5} / 1.8×10^{-5} = **2.8**

Make a buffer with **0.28 moles of acid and 0.10 moles of conjugate base**, water to make 1.0 L

Diluting a buffer solution will not change the pH – see book for discussion

pH = pKa + log ([conjugate base] / [acid]) = pKa + log (Moles/L ⁄ Moles/L)   Moles/L cancel out

Example 18.5 Buffer maintain a pH
A. ? is pH change when 1.00 ml of 1.00 M HCl is added to 1.000 L of pure water

B. ? is pH change when it is added to 1.000 L of buffer contained 0.700 M CH_3COOH and 0.600 M of CH_3COO^-

A. pH = - log ($[H_3O^+]$)   We need the $[H_3O^+]$ Note: V2 = 1.00 ml + 1.000 L = 1.001 L

M1V1 = M2V2   M2 = M1V1/V2 = 1.00 M * [1.00 ml * 1 L / (1000 ml)] / 1.001 L = 9.99×10^{-4} M

pH = - log ($[H_3O^+]$) = - log (9.99×10^{-4}) = **3.00**

B. Moles of HCl = 1.00 M * 1.00 ml * 1 L / 1000 ml = 0.00100 Mole

Note: All of the HCl will react as it's a much stronger acid than CH_3COOH

	H_3O^+	+	CH_3COO^-	⇄	CH_3COOH + HOH	
Initial	0.00100		0.600		0.700	
Change	-0.00100		-0.00100		+0.00100	
Mol after Reaction	0		0.599		0.701	divide by 1.001 L
Concentration [x]	0		0.598		0.700	Volume is now 1001 ml

	CH_3COOH + HOH	⇄	H_3O^+ +	CH_3COO^-
Initial	0.700		0	0.598
Change	-x		+x	+x
Equilibrium	0.700 – x		x	x + 0.598

Ka = 1.8×10^{-5} = [CH_3COO^-] [H_3O^+] /[CH_3COOH] = x (<u>x</u> + 0.598) / (0.700 –<u>x</u>)

Since Ka is small, **assume (<u>x</u> + 0.598) = 0.598 and (0.700 –<u>x</u>) = 0.700**

Ka = 1.8×10^{-5} = 0.598 x / 0.700   **x = 0.700 * 1.8×10^{-5} / 0.598 = 2.1 x 10^{-5}**

Prove Assumption (<u>x</u> + 0.598) = (2.1×10^{-5} + 0.598) = 0.598 Assumption is True

pH = - log (H_3O^+) = - log (2.1×10^{-5}) = **4.68**

So 1 ml of 1.00 M HCl into 1.000 L of pure water changes pH from 7.00 to 3.00,
1 ml of 1.00 M HCl into 1.000 L of a buffer changes the pH from 7.00 to 4.68. **The buffer works!**

STUDENTS ANSWER
Review Check 18.2   1. Which choice would make a good buffer and why?

   A. 0.20 M HCN and 0.10 M KCN   C. 0.20 M CH3COOH and 0.10 M HCOOH

   B. 0.20 M HCl and 0.10 M KOH   D. 0.10 M HCl and 0.010 M KCl

2. If an acetic acid/sodium acetate buffer solution is prepared from 100 ml of 0.10 M acetic acid,

what volume of 0.10 M sodium acetate must be added to have a pH of 4.00?

3. What is the pH of a buffer composed of 100 ml of 0.20 M NH4Cl and 200 ml of 0.10 M NH3?
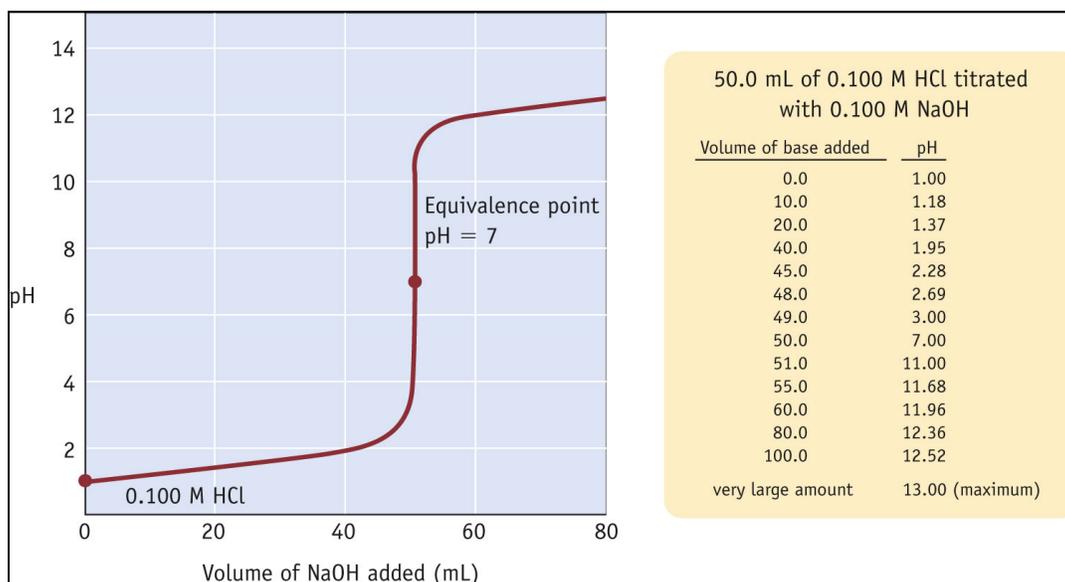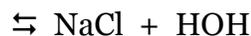
18.3 Acid-Base Titrations

   The pH at the equivalence point of a strong acid vs a strong base titration is pH = 7

   The pH of a weak acid vs a strong Base is pH > 7

   The pH of a strong acid vs a weak base pH < 7
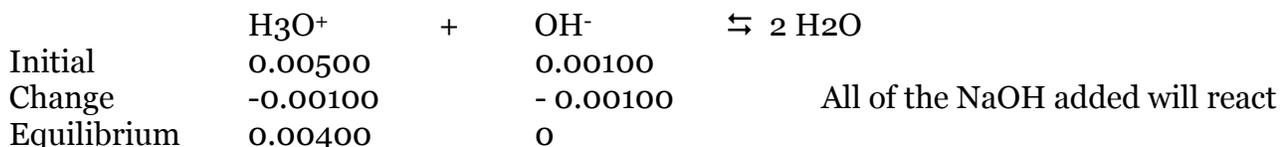
Strong Acid vs Strong Base   HCl + NaOH $\leftrightarrows$ NaCl + HOH

               Net Ionic Equation H3O$^+$ + OH$^-$ $\leftrightarrows$ 2 HOH

50.0 mL of 0.100 M HCl titrated with 0.100 M NaOH	
Volume of base added	pH
0.0	1.00
10.0	1.18
20.0	1.37
40.0	1.95
45.0	2.28
48.0	2.69
49.0	3.00
50.0	7.00
51.0	11.00
55.0	11.68
60.0	11.96
80.0	12.36
100.0	12.52
very large amount	13.00 (maximum)

Adding 0.100 M NaOH to 0.100 M HCl

A. pH of the initial solution.   **pH** = - log (H3O$^+$) = - log (0.100) = **1.00**

B. pH before equivalence point, when 10.0 ml 0.100 M NaOH is added to 50.0 ml 0.100 M HCl

   Moles NaOH = Molarity * Volume = 0.100 (10.0 ml * 1 L / 1000 ml) = 0.00100 M

   Moles of HCl = Molarity * Volume = 0.100 (50.0 ml * 1 L / 1000 ml) = 0.00500 M

	H3O$^+$	+	OH$^-$	$\leftrightarrows$ 2 H2O
Initial	0.00500		0.00100	
Change	-0.00100		- 0.00100	All of the NaOH added will react
Equilibrium	0.00400		0	

We have 0.00400 Moles of H_3O^+ in 60.0 ml of solution

Molarity of H_3O^+ is 0.00400 Moles * 1000 ml / 60.0 ml * 1 L = 0.0667 M

pH = - log (H_3O^+) = - log (0.0667) == - log (6.67 x 10^{-2}) **1.176**

Student run off the math to show when 49.5 ml of NaOH solution is added, the pH is 3.3

C. pH at the equivalence point.

50.0 ml of 0.100 M NaOH is added to 50.0 ml of 0.100 M HCl. All of the Base and acid are neutralized. Therefore the pH is 7

D. pH just after the equivalence point. 55.0 ml 0.100 M NaOH added to 50.0 ml 0.100 M HCl

Moles of NaOH = Molarity * Vol = 0.100 M * 55.0 ml * 1 L / 1000 ml = 0.00550 Mol

Moles of HCl = Molarity * Volume = 0.100 (50.0 ml * 1 L / 1000 ml) = 0.00500

	H_3O^+	+	OH^- ⇆	2 HOH
Initial	0.00500		0.00550	
Change	-0.00500		-0.0050	
Mol after Reaction	0		0.00050	
Concentration [x]	0		0.00050 / (50+55 ml * 1L/1000 ml) = 0.00476 M	

pOH = - log (OH^-) = - log (0.00476) = - log (4.76 x 10^{-3}) = **2.322**

pH = 14.00 − pOH = 14.00 − 2.322 = **11.678**

Weak Acid with a Strong Base   Titrate 100.0 ml of 0.100 M Acetic Acid with 0.100 M NaOH
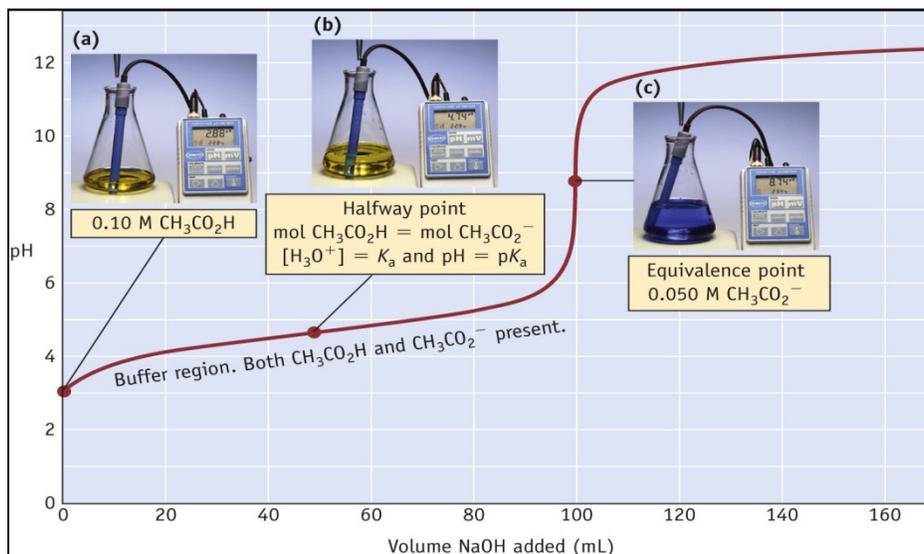
A. pH before the titration begins

pH is from weak acid Ka and acid concentration – see also IE 17.5.

100.0 ml * 0.100 M * 1 L / 1000 ml = 0.0100 Moles CH3COOH

	CH3COOH + HOH ⇆	CH3COO$^-$ +	H_3O^+
Initial	0.0100	0	0
Change	-x	+x	+x
Equilibrium	0.0100 − x	x	x

$Ka = [CH_3COO^-] [H_3O^+] / [CH_3COOH] = 1.8 \times 10^{-5} = x^2 / (0.0100 - \underline{x})$

Since Ka is small, **Assume** $(0.0100 - \underline{x}) = 0.0100$

$1.8 \times 10^{-5} = x^2 / 0.0100$ $x^2 = 1.8 \times 10^{-5} \times 0.0100$ $\mathbf{x = 4.24 \times 10^{-4}}$

Prove Assumption $(0.0100 - x) = (0.0100 - 4.24 \times 10^{-4}) = 0.0100$ **Assumption is True**

$\mathbf{pH} = - \log (H_3O^+) = - \log (4.24 \times 10^{-4}) = \mathbf{3.37}$

B. pH when ½ of the Acetic Acid is neutralized.

$$CH_3COOH + HOH \leftrightarrows CH_3COO^- + H_3O^+$$

Initial	0.0100	0	0
Change	-0.0500	+0.0500	+0.0500
Equilibrium	0.0500	0.0500	0.0500

$pKa = \log (1.8 \times 10^{-5}) = 4.74$

$\mathbf{pH} = pKa + \log ([\text{conjugate base}] / [\text{weak acid}]) = 4.74 + \log (0.0500/0.0500) = \mathbf{4.74}$

Or another way to do it:

$$CH_3COOH + OH^- \leftrightarrows CH_3COO^- + H_2O$$

Initial	0.0100	+0.0500	0	0
Change	-0.0500	-0.0500	+0.0500	+0.0500
Equilibrium	0.0500	0	0.0500	0.0500

$\mathbf{pH} = pKa + \log ([\text{conjugate base}] / [\text{weak acid}]) = 4.74 + \log (0.0500/0.0500) = \mathbf{4.74}$

C. Closer to the end point, from Interactive Example 18.6

(a) What is the pH when 90.0 ml of the 0.100 M NaOH is added

Calculate the amounts of material after all of the 90.0 ml of NaOH is reacted

$90.0 \text{ ml} \times 1L \times 0.100 \text{ M} / 1000 \text{ ml} = 0.00900 \text{ Moles NaOH}$

$$CH_3COOH + OH^- \leftrightarrows CH_3COO^- + H_2O$$

Start	0.0100	0.00900	0
Change	-0.00900	-0.00900	+0.00900
After Reaction	0.0010	0	0.00900

$pH = pKa + \log ([\text{conjugate base}] / [\text{weak acid}]) = 4.74 + \log (0.00900/0.0010) = 4.74 + 0.95$

$\mathbf{pH = 5.69}$

D. After the end point: ? pH after 110.0 ml of NaOH is added?

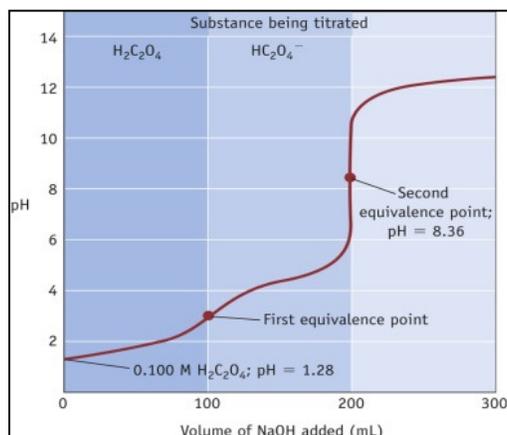Note: Moles NaOH $= 110.0 \text{ ml} \times 1L \times 0.100 \text{ M} / 1000 \text{ ml} = 0.01100 \text{ Moles}$

$$CH_3COOH + OH^- \leftrightarrows CH_3COO^- + H_2O$$

Initial	0.0100	0.01100	0
Change	-0.0100	-0.0100	0.0100
After Reaction	0	0.00100	0.0100

Most of the pH is from the [OH-] and very little from the reaction of Acetate with water
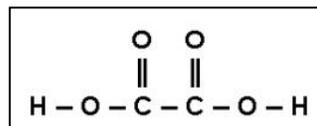
$[OH^-] = \text{Moles/Liter} = 1.00 \times 10^{-3} / (100 \text{ ml} + 110 \text{ ml}) \times 1L / 1000 \text{ ml} = 4.76 \times 10^{-3} \text{ M}$

So: $\mathbf{pH} = 14.0 - \log ([OH^-]) = 14.00 - \log (4.76 \times 10^{-3}) = 14.00 - 2.32 = \mathbf{11.68}$
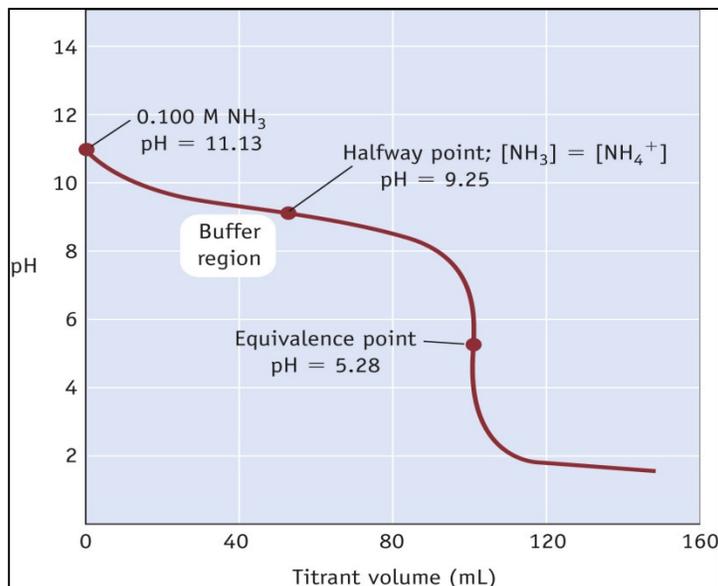
Titration of Weak Polyprotic Acids

Weak Polyprotic Acids will have two break points, one for the equivalence point for each proton loss:

$$HOOC\text{-}COOH + HOH \rightleftharpoons HOOC\text{-}COO^- + H_3O^+ \quad Ka_1 = 5.9 \times 10^{-2}$$

$$HOOC\text{-}COO^- + HOH \rightleftharpoons {}^-OOC\text{-}COO^- + H_3O^+ \quad Ka_2 = 6.4 \times 10^{-5} \quad \text{Oxalic Acid}$$

Titration of a Weak Base with a Strong Acid

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + HOH \qquad \text{Titrate 100.0 ml of 0.100 M NH3 with 0.100 M HCl}$$

a. What is Initial pH

	NH3 +	H2O ⇌	NH4+ +	OH-
Start	0.100		0	0
Change	-x		+x	+x
Equilibrium	0.100-x		x	x

$Kb = [OH^-][NH_4^+]/[NH_3] = 1.8 \times 10^{-5} = x * x / (0.100 - \underline{x})$

Kb is small, **Assume** $(0.100 - \underline{x}) = 0.0100$

$1.8 \times 10^{-5} = x * x / 0.100 \qquad x^2 = 1.8 \times 10^{-5} * 0.100 = 1.8 \times 10^{-6} \quad \mathbf{x = 1.34 \times 10^{-3}}$

Prove Assumption $(0.0100 - x) = (0.0100 - 0.00134) - 0.0100$ **Assumption is True**

$[OH^-] = x = 1.34 \times 10^{-3}$ $pOH = 2.87$ $pH = 14.00 - pOH = 11.13$

B. At the halfway point $[NH_3] = [NH_4^+]$

pKa of $5.6 \times 10^{-10} = -\log(5.6 \times 10^{-10}) = 9.2$

pH = pKa + log ([conjugate base] /[weak acid]) $= 9.2 + \log([NH_4^+] / [NH_3]) = 9.2 + \log(1) = \mathbf{9.2}$

Example 18.7   ? is the pH at the equivalence point

Moles of HCl = Moles of NH_3 = see above = 0.0100 Moles

	NH3 +	H3O+ ⇆	NH4+ + H2O
Initial	0.0100	0.0100	0
Change	-0.0100	-0.0100	+0.0100
After Reaction	0	0	0.0100

Concentration []   0.0100 Mole * 1000 ml / (100 ml + 100 ml) * 1 L = **0.0500 M**

Now, take this NH_4^+ and see how it reacts with water

	NH4+ + H2O ⇆	NH3 +	H3O+
Initial	0.0500	0	0
Change	-x	+x	+x
Equilibrium	0.0500 – x	x	x

$Ka = [NH_3][H_3O^+] / [NH_4^+] = 5.6 \times 10^{-10} = x * x / (0.0500 - \underline{x})$
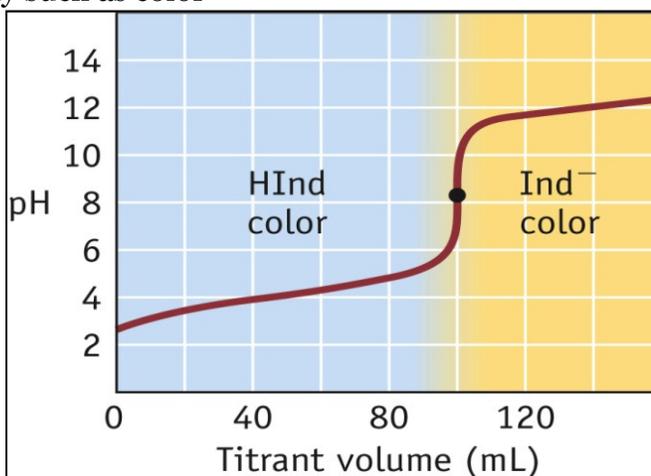
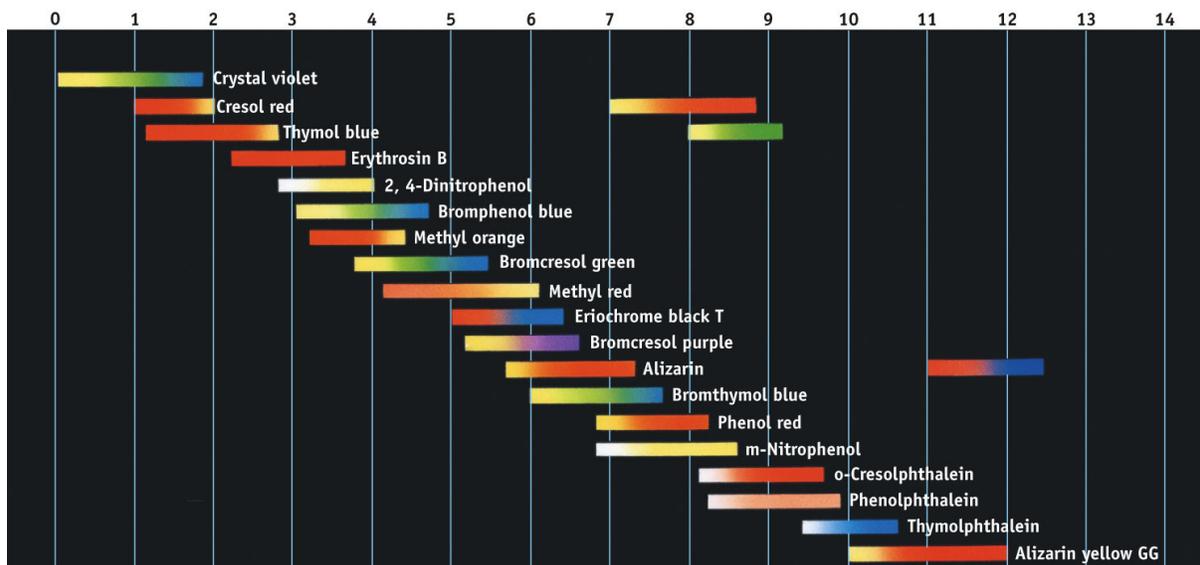Since Ka is small, **Assume** $(0.0100 - \underline{x}) = 0.0500$

$5.6 \times 10^{-10} = x^2 / 0.0500$ $x^2 = 5.6 \times 10^{-10} * 0.0500$ $x = \mathbf{5.29 \times 10^{-6}}$

Prove Assumption $(0.0100 - \underline{x}) = (0.0100 - 5.29 \times 10^{-6}) = 0.0100$ **Assumption is True**

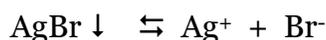$pH = -\log(H_3O^+) = -\log(5.29 \times 10^{-6}) = \mathbf{5.28}$

pH Indicators as used in titrations, <u>Hind</u>, is a substance used to signal the equivalence point of a titration by a change in some physical property such as color

Hind + H2O ⇆ H3O+ + Ind-

18.4 Solubility of Salts

Solubility Product Constant Ksp   Solubility is in Moles/Liter, 100 ml or other units

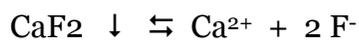$AgBr \downarrow \leftrightarrows Ag^+ + Br^-$ (Solubility 7.35×10^{-7} M for each ion)

$Ksp = [Ag^+][Br^-] = [7.35 \times 10^{-7}][7.35 \times 10^{-7}] = 5.40 \times 10^{-13}$

$A_xB_y \downarrow \leftrightarrows x\, A^{y+} + y\, B^{x-}$ **$Ksp = [A^{y+}]^x\ [B^{x-}]^y$**

$CaF2 \downarrow \leftrightarrows Ca^{2+} + 2\,F^-$ $Ksp = [Ca^{2+}][F^-]^2$ $= 5.3 \times 10^{-11}$
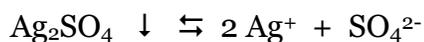
$Ag_2SO_4 \downarrow \leftrightarrows 2\,Ag^+ + SO_4{}^{2-}$ $Ksp = [Ag^+]^2[SO_4{}^{2-}]$ $= 1.2 \times 10^{-5}$

Table 18.2 Some Common Insoluble Compounds and Their K_{sp} Values*

Formula	Name	K_{sp} (25 °C)	Common Names/Uses
$CaCO_3$	Calcium carbonate	3.4×10^{-9}	Calcite, iceland spar
$MnCO_3$	Manganese(II) carbonate	2.3×10^{-11}	Rhodochrosite (forms rose-colored crystals)
$FeCO_3$	Iron(II) carbonate	3.1×10^{-11}	Siderite
CaF_2	Calcium fluoride	5.3×10^{-11}	Fluorite (source of HF and other inorganic fluorides)
$AgCl$	Silver chloride	1.8×10^{-10}	Chlorargyrite
$AgBr$	Silver bromide	5.4×10^{-13}	Used in photographic film
$CaSO_4$	Calcium sulfate	4.9×10^{-5}	Hydrated form is commonly called *gypsum*
$BaSO_4$	Barium sulfate	1.1×10^{-10}	Barite (used in "drilling mud" and as a component of paints)
$SrSO_4$	Strontium sulfate	3.4×10^{-7}	Celestite
$Ca(OH)_2$	Calcium hydroxide	5.5×10^{-5}	Slaked lime

* The values in this table were taken from *Lange's Handbook of Chemistry,* 15th edition, McGraw-Hill Publishers, New York, NY (1999). Additional K_{sp} values are given in Appendix J.

Solubility and Ksp
Interactive Example 18.8   Calculate the Ksp for Calcium Fluoride if Ca^{2+} is 2.3×10^{-4} mol/L

$CaF_2 \downarrow \leftrightarrows Ca^{2+} + 2\,F^-$ $Ksp = [Ca^{2+}][F^-]^2$

For every one mole of CaF_2 that dissolves, 1 mole of Ca^{2+} is formed and 2 moles of F^- is formed

$[F^-] = 2\,[Ca^{2+}] = 2\,[2.3 \times 10^{-4}] = 4.6 \times 10^{-4}$

$Ksp = [Ca^{2+}][F^-]^2 = [2.3 \times 10^{-4}][4.6 \times 10^{-4}]^2 = 4,9 \times 10^{-11}$

Now change the problem around and using Ksp, calculate the solubility of an ion

Interactive Example 18.9   Ksp for BaSO4 is 1.1×10^{-10}, what is its solubility in moles & g/L

	$BaSO_4 \downarrow \leftrightarrows$	Ba^{2+} +	SO_4^{2-}
Initial		0	0
Change		+x	+x
Equilibrium		x	x

   Ksp = $[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10} = x * x = x^2$ x = 1.05×10^{-5} = **1.1×10^{-5} = Moles/L**

   1.1×10^{-5} = Moles/L * 233 g/Mole = **2.4×10^{-3} g/L**

Example 18.10   Ksp for MgF2 is 5.2×10^{-11}, what is the solubility of the salt in moles & g/L

	$MgF_2 \downarrow \leftrightarrows$	Mg^{2+} +	$2 F^{2-}$
Initial		0	0
Change		+x	+2x
Equilibrium		x	2x

   Ksp = $[Mg^{2+}][2 F^{2-}]^2 = 5.2 \times 10^{-11} = x * (2x)^2 = 4 x^3$ x = 2.35×10^{-4} =**2.4×10^{-4} = Moles/L**

   2.4×10^{-4} = Moles/L * 62.3 g/Mole = **1.5×10^{-2} g/L**

Relative Solubility's   AgCl $\downarrow$ $\leftrightarrows Ag^+ + Cl^-$ Ksp = 1.8×10^{-10}

But $Ag_2CrO_5 \downarrow$ $\leftrightarrows 2 Ag^+ + CrO_5^{2-}$ Ksp = 9.0×10^{-12}

Ya'd think the AgCl is more soluble, but – work it out:

	AgCl $\downarrow$	$\leftrightarrows$	Ag^+ +	Cl^-
Initial			0	0
Change			+x	+x
Equilibrium			x	x

   Ksp = $[Ag^+][Cl^-] = 1.8 \times 10^{-10} = x * x$ x = 1.34×10^{-5} = **1.3×10^{-5} Moles / L**

	$Ag_2CrO_5 \downarrow$	$\leftrightarrows$	$2 Ag^+$ +	CrO_5^{2-}
Initial			0	0
Change			+2x	+x
Equilibrium			2x	x

   Ksp = $[2 Ag^+]^2 [CrO_5^2] = 9.0 \times 10^{-12} = (2x)^2 x = 4 x^3$ **x = 1.3×10^{-4} Moles / L**

Solubility and the Common Ion

What happens if we add some Silver ions (Silver Nitrate) to a saturated solution of Silver Acetate?

       $AgCH3COO \downarrow \leftrightarrows Ag^+ + CH3COO^-$
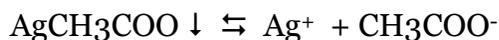
Le Chatelier's principal says the reaction will shift to the left so more Silver Acetate will ppt out

Example 18.11   Saturated AgCl in 1.00 L of 0.55 M NaCl ? AgCl will dissolve?

	AgCl $\downarrow \leftrightarrows$	Ag^+	+	Cl^-
Initial	∞			0.55
Change		+x		+x
Final		x		0.55 + x

$Ksp = 1.8 \times 10^{-10} = x * (0.55 + x)$

Ksp is small, **Assume** $(0.55 + x) = 0.55$, or solve the Quadratic

$1.8 \times 10^{-10} = 0.55\, x$ $x = 3.27 \times 10^{-10} = \mathbf{3.3 \times 10^{-10}}$

Prove Assumption $(0.55 - 3.3 \times 10^{-10}) = 0.55$ **Assumption is True**

Wt AgCl in grams = Moles * Mw = 3.3×10^{-10} Moles * 143 g/Mole = $\mathbf{4.7 \times 10^{-8}}$ **g AgCl**

Student – calculate the solubility of AgCl in pure water, without adding the NaCl

Effect of a Basic Anion on Salt Solubility

Any salt containing an Anion that is the Conjugate Base of a weak acid will dissolve in water to a greater extent than given by Ksp. These salts will dissolve in strong acids. This includes salts of
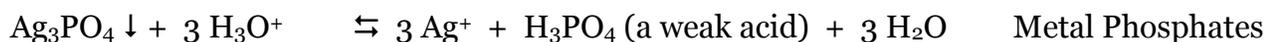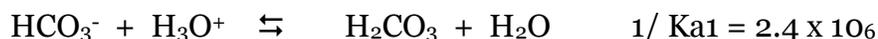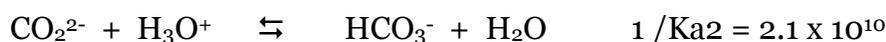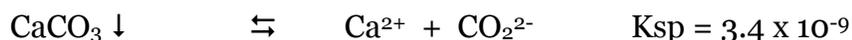
Phosphate (PO_4^{3-})   Acetate (CH_3-COO^-)

Carbonate (CO_3^{2-})   Cyanide (CN^-)   Sulfide ($S2^-$)

$PbS \downarrow \leftrightarrows Pb^{2+} + S^{2-}$ $S^{2-} + H_2O \leftrightarrows HS^- + OH^-$ $Kb = 1 \times 10^5$

$CaCO_3 \downarrow$ $\leftrightarrows$ $Ca^{2+} + CO_2^{2-}$ $Ksp = 3.4 \times 10^{-9}$

$CO_2^{2-} + H_3O^+$ $\leftrightarrows$ $HCO_3^- + H_2O$ $1 / Ka2 = 2.1 \times 10^{10}$

$HCO_3^- + H_3O^+$ $\leftrightarrows$ $H_2CO_3 + H_2O$ $1/ Ka1 = 2.4 \times 10_6$

H_2CO_3 $\leftrightarrows$ $CO^2 \uparrow + H^2O$ $K = 10^5$ You can see the CO2 Bubbles

$FeS \downarrow + 2\, H_3O^+ \leftrightarrows$ $Fe^{2+} + H_2S \uparrow + 2\, H_2O$ Metal Sulfides in strong acids

$Ag_3PO_4 \downarrow + 3\, H_3O^+$ $\leftrightarrows 3\, Ag^+ + H_3PO_4$ (a weak acid) $+ 3\, H_2O$ Metal Phosphates

$Mg(OH)_2 \downarrow + 2\, H_3O^+$ $\leftrightarrows Mg^{2+} + 4\, H_2O$ Metal Hydroxides

Salts are not soluble if the anion is a conjugate base of a strong acid:

$AgCl \downarrow \leftrightarrows Ag^+ + Cl^-$ $Ksp = 1.8 \times 10^{-10}$

$H_3O^+ + Cl^- \leftrightarrows HCl + H_2O$ $K << 1$ Is very very small as HCl + H2O is very very large

18.5 Precipitation Reactions   Ksp and Q

$AgCl \downarrow \leftrightarrows Ag^+ + Cl^-$ $Ksp = 1.8 \times 10^{-10}$

At Equilbrium $Ksp = [Ag^+]\,[Cl^-]$

If not at Equilibrium $\mathbf{Qsp} = [Ag^+]\,[Cl^-]$
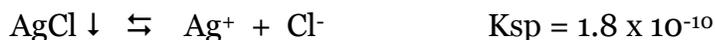
If $Q = K$ The solution is at Equilibrium and is a Saturated Solution

      $Q < K$ The solution is not Saturate

      $Q > K$ The solution is Super Saturated and precipitation will occur.
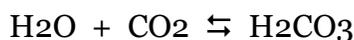
CO2 and the Ocean:

Over the past 200 Years, the oceans have absorbed 550 Billion (550,000,000,000) Tons of CO2

Currently absorbing 22 Million (22,000,000) Tons of CO2 DAY

All the man-made carbon:

Would increase the amount of CO2 by 20% if not absorbed by the ocean

Would raise the temp of the earth by 2 $^{\circ}$C

CO2 dissolved in the ocean forms a weak acid – Carbonic Acid

$H_2O + CO_2 \leftrightarrows H_2CO_3$

This acid can dissolve the $CaCO_3$ shells of marine life – see above equation

Interactive Example 18.13   AgCl is placed in a beaker of water. After some time, Ag^+ and Cl^- are measured at 1.2×10^{-5} mol/L. Is the system at equilibrium?

$Qsp = [Ag^+][Cl^-] = [1.2 \times 10^{-5}][1.2 \times 10^{-5}] = 1.4 \times 10^{-10}$

$Ksp = 1.8 \times 10^{-10}$ $Qsp < Ksp$, the solution is NOT at equilibrium

Ksp, Precipitation Reactions
Will a precipitate occur? What concentrations of ions are required to from a ppt?

$[Mg^{2+}] = 1.5 \times 10^{-6}$ M, NaOH is added to make OH^- 1.0×10^{-4} M. $Mg(OH)_2$ $Ksp = 5.6 \times 10^{-12}$.
If there is no ppt, will it occur if [OH-] is increased to 1.0×10^{-2} M?

$Mg(OH)_2 \downarrow \leftrightarrows Mg^{2+} + 2 OH^-$

$Qsp = [Mg^{2+}][OH^-]^2 = [1.5 \times 10^-][1.0 \times 10^{-4}]^2 = 1.5 \times 10^{-14}$

$Qsp = 1.5 \times 10^{-14} < Ksp = 5.6 \times 10^{-12}$.   No ppt will form

$Qsp = [Mg^{2+}][OH^-]^2 = [1.5 \times 10^-][1.0 \times 10^{-2}]^2 = 1.5 \times 10^{-10}$

$Qsp = 1.5 \times 10^{-10} > Ksp = 5.6 \times 10^{-12}$.   A ppt will form!

Interactive Example 18.14   Ion concentration required to begin ppt

A. $[Ba^{2+}]$ is 0.010 M. How much SO_4^{2-} is required to start ppt formation?

$BaSO_4 \downarrow \leftrightarrows Ba^{2+} + SO_4^{2-}$ $Ksp = 1.1 \times 10^{-10} = [SO_4^{2-}][Ba^{2+}]$

$[SO_4^{2-}] = Ksp / [Ba^{2+}] = 1.1 \times 10^{-10} / 0.010 = 1.1 \times 10^{-8}$ M

**B.** When the [Sulfate] is 0.015 M, what is the [Barium] ?

$[Ba^{2+}] = Ksp / [SO_4^{2-}] = 1.1 \times 10^{-10} / 0.015 = 7.3 \times 10^{-9}$ M

Students read and understand Example 18.15   Will a ppt occur?

18.6 Equilibrium with Complex Ions
Add Ni^{2+} to water and you form a Ligand of $[Ni(H_2O)_6]^{2+}$ The negative end of the polar water molecules ligh up with the positive metal ion. If you add Ammonia (NH_3), the water is displace by
$NH_3 \rightarrow [Ni(NH_3)_6]^{2+}$ K_f is a Formation Constant
$Cu^{2+} + 4 NH_3 \leftrightarrows [Cu(NH_3)_4]^{2+}$ $K_f = 2.1 \times 10^{13}$
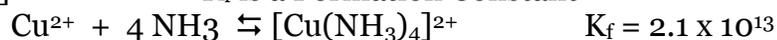
Example 18.16   Complex Ion Equilibria

? $[Cu^{2+}]$ in 0.00100 mole of CuCpx added to 1.00 L of 1.50 M HN_3? $K_f = 2.1 \times 10^{13}$

$$[Cu(NH_3)_4]^{2+} \leftrightarrows Cu^{2+} + 4\, NH_3$$

	$[Cu(NH_3)_4]^{2+}$	Cu^{2+}	$4\,NH_3$
Initial	0.00100	0	1.50 – (4 * 0.00100)
Change	-x	+x	+4x
Equilibrium	0.00100 – x	x	1.50 – 0.00400 + 4x

$K_d = 1/K_f = [Cu^{2+}]\,[NH3]^4 / [[Cu(NH_3)_4]^{2+}] = 1/2.1 \times 10^{13} = x\,(1.50 - 0.00400 + 4x)^4 / (0.00100 - x)$

Since K_f is very large, x is very small and $(1.50 - 0.00400 + \underline{4x}) = 1.50$ and $(0.00100 - \underline{x}) = 0.0010$

$1 / 2.1 \times 10^{13} = x\,(1.50)^4 / (0.00100)$ $x = 9.4 \times 10^{-18}$

Prove Assumption $(0.00100 - x) = (0.00100 - 9.4 \times 10^{18}) = 0.00100$ **Assumption is True**

18.7 Solubility of Complex Ions

AgCl does not dissolve in water or a strong acid. It does dissolve in Ammonia

$AgCl \downarrow + 2\, NH3 \qquad \leftrightarrows [Ag(NH_3)_2]^+ + Cl^-$

$AgCl \downarrow \qquad\qquad \leftrightarrows Ag^+ + Cl^- \qquad\qquad Ksp = 1.8 \times 10^{-10}$

$Ag^+ + 2\, NH3 \qquad \leftrightarrows [Ag(NH_3)_2]^+ \qquad\qquad K_f = 1.1 \times 10^7$

$K_{net} = K_{sp} * K_f = 1.8 \times 10^{-10} * 1.1 \times 10^7 = 2.0 \times 10^{-3} = [Ag(NH_3)_2]^+\,[Cl^-] / [NH3]^2$

| (a) AgCl precipitates on adding NaCl(aq) to AgNO₃(aq). | (b) The precipitate of AgCl dissolves on adding aqueous NH₃ to give water-soluble [Ag(NH₃)₂]⁺. | (c) The silver-ammonia complex ion is changed to insoluble AgBr on adding NaBr(aq). | (d) Solid AgBr is dissolved on adding Na₂S₂O₃(aq). The product is the water-soluble complex ion [Ag(S₂O₃)₂]³⁻. |

AgCl(s), $K_{sp} = 1.8 \times 10^{-10}$ — $[Ag(NH_3)_2]^+(aq)$ —   AgBr(s), $K_{sp} = 5.4 \times 10^{-13}$ — $[Ag(S_2O_3)_2]^{3-}(aq)$

Example 18.17 Complex Ions Solubility

? is K_{net} for dissolving AgBr in a solution of Thiosulfate, $S_2O_3{}^{2-}$

$AgBr \downarrow \leftrightarrows Ag^+ + Br^- \qquad\qquad K_{sp} = 5.0 \times 10^{-13}$

$Ag^+ + 2\, S_2O_3{}^{2-} \leftrightarrows [Ag(S_2O_3)_2]^{3-} + Br^- \qquad K_f = 2.9 \times 10^{13}$

Net $AgBr \downarrow 2\, S_2O_3{}^{2-} \leftrightarrows [Ag(S_2O_3)_2]^{3-} + Br^- \qquad K_{net} = K_{sp} * K_f = 15$
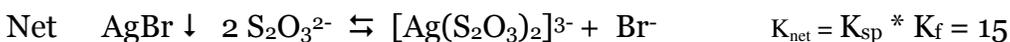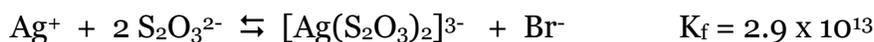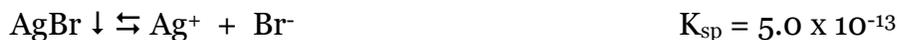
Book Reactions that you need to be able to solve for Ch 18

18.1 Prove pH of Acetic Acid

Add Sodium Acetate to Acetic Acid, ? pH

IE 18.1 NaOH and Lactic Acid   NaOH Limiting reactant

IE 18.2 Acetic Acid and Sodium Hydroxide

IE 18.3 Benzoic Acid and Sodium Benzoate   Henderson-Hasselbalch Equation

IE 18.4 Preparing a Buffer Solution   Pick the compounds, calculate ratio

IE 18.5 Buffer Maintains a pH   HCl in water then in Acetate buffer

Strong Acid vs Strong Base   HCl vs NaOH
    A. pH of initial solution
    B. pH before the equivalence point
    C. pH at the equivalence point
    D. pH just after the equivalence point

IE 18.6 Weak Acid vs Strong Base   Acetic Acid vs NaOH
    A. pH before the titration begins   *I don't get same answer as book, use book*
    B. pH when ½ the Acetic Acid is neutralized
    C. pH when 90.0 ml of NaOH is added

IE 18.7 Titrate of Weak Base with Strong Acid NH_3 with HCl
    A. pH Initial   *Not in book, you need to work this one out*
    B. At half way point

IE 18.8 Ksp for CaF_2

IE 18.9 Given Ksp, calculate solubility in g/L

IE 18.10 Given Ksp, calculate solubility in g/L

Relative Solubility of AgCl vs Ag_2CrO_5

Ex 18.11 Saturated AgCl and NaCl

IE 18.13 AgCl in a beaker over time, Q

$Mg(OH)_2$ Qsp precipitation

IE 18.14 Ion concentration to begin ppt

IE 18.15 Ksp and precipitation

IE 18.17 Complex Ion Solubility