

UNIT 9 – CHAPTER 15 STUDENT NOTES: ACID-BASE EQUILIBRIUM AND THE SOLUBILITY PRODUCT

Common ion effect – The shift in equilibrium position that occurs because of the addition of an ion already involved in the equilibrium.

EX 1: Calculate the pH of the following solutions

- a) 1.0 M HF $K_a = 7.2 \times 10^{-4}$
 b) 1.0 M HF and 1.0 M NaF

Buffered solution – a solution that resists a pH change when $[OH^-]$ or $[H^+]$ are added

- Weak acid and its salt
- Weak base and its salt

EX 2: Calculate the pH of a 0.50 M $HC_2H_3O_2$ and 0.50 M solution of $NaC_2H_3O_2$ buffer solution.

EX 3: Calculate the pH of the solution in the above example when 0.010 moles of NaOH are added.

EX 4: Calculate the solution of

- a) 500 mL of 0.250 M $HCOOH$ and 0.100 M $NaCOOH$ solution

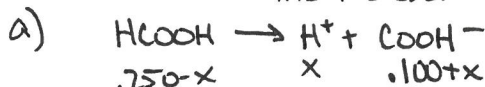
$\rightarrow$ M.S. = $HCOOH, Na^+, COOH^-$

$K_a = 1.8 \times 10^{-4}$

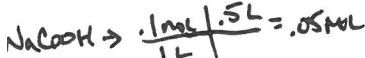
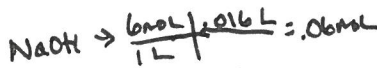
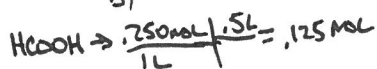
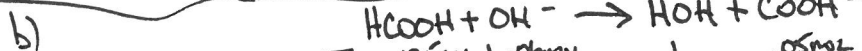
- b) the above solution with 10 mL of a 6.00 M NaOH solution

$\rightarrow$ M.S. = $HCOOH, Na^+, COOH^-, Na^+, OH^-$

500 mL OF EACH TOTAL 1 L SOLN

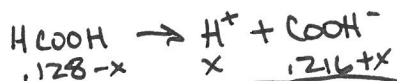


$K_a = \frac{[H^+][COOH^-]}{[HCOOH]} \rightarrow x = 4.5 \times 10^{-4} \rightarrow \boxed{PH = 3.4}$



I	.125 M	.100 M	.05 M
C	-.06	-.06	+.06
E	.065 M	.04 M	.11 M
	.51 L TOTAL = .128 M		.51 L TOTAL = .216 M

STEP 1: "EAT UP" ACID



$K_a = 1.8 \times 10^{-4} = \frac{[H^+][COOH^-]}{[HCOOH]} \rightarrow x = 1.1 \times 10^{-4}$

$\boxed{PH = 3.96}$

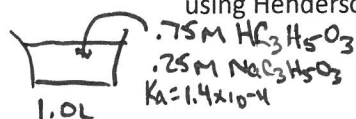
STEP 2: DISSOCIATE

Henderson-Hasselbalch equation – used to solve buffer problems

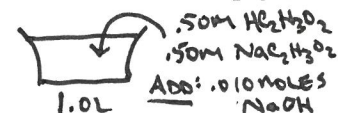
$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

OR: $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$

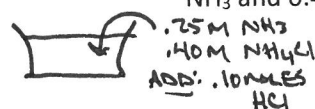
EX 5: Calculate the pH of a 0.75 M lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) and 0.25 M sodium lactate ($\text{NaC}_3\text{H}_5\text{O}_3$) solution using Henderson-Hasselbalch. ($K_a = 1.4 \times 10^{-4}$)



EX 6: Using Henderson-Hasselbalch, calculate the a) pH of a 0.50 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.50 M solution of $\text{NaC}_2\text{H}_3\text{O}_2$ buffer solution (from EX 2). Then b) when 0.010 moles of NaOH are added. ($K_a = 1.8 \times 10^{-5}$)



EX 7: Calculate the pH of a solution that results when 0.10 moles of HCl is added to 1.0 liter of a 0.25 M NH_3 and 0.40 M NH_4Cl . ($K_b = 1.8 \times 10^{-5}$)



STEP 1: H^+ "EATS UP" NH_3

$$\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$$

I	.25	.1	.40
C	-.1	-.1	+.1
E	.15 mol	0	.50 mol

STEP 2: DISSOCIATE $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$

$$K_b = 1.8 \times 10^{-5} = \frac{(.15-x)(.50+x)}{(.15+x)}$$

$$x = 5.4 \times 10^{-6} \rightarrow \text{pOH} = 5.27$$

$\text{pH} = 8.73$

HENDERSON-HASSELBALCH

$$\text{pH} = \text{p}K_a + \log \frac{[\text{BASE}]}{[\text{ACID}]}$$

$$\text{pH} = 9.25 + \log \frac{[.25]}{[.50]}$$

$$\text{pH} = 9.25 + (-.52)$$

$$\boxed{\text{pH} = 8.73}$$

EX 8: You prepare a buffer solution of 0.323 M NH_3 and $(\text{NH}_4)_2\text{SO}_4$. What molarity is necessary to have a pH of 8.6? The K_b for NH_3 is 1.8×10^{-5} .

$\rightarrow \geq \text{NH}_4^+$!

Titrations and pH curves

Titration – reaction of an acid and base

The process of an acid-base titration is often monitored by plotting the pH of a solution being analyzed as a function of the amount of titrant added. Such a plot is called a pH curve or titration curve.

Strong acid-strong base titration

50.0 mL of 0.200 M HNO_3 and add 0.100 M NaOH

a) No added NaOH

d) 50 mL (total) NaOH

b) 10 mL of NaOH added

e) 100 mL (total) NaOH

c) 20 mL (total) NaOH

f) 150 mL (total) NaOH

At end point there is a dramatic change.

Before – large $[\text{H}^+]$, $[\text{OH}^-]$ has little pH change

At the end point – small $[\text{H}^+]$, $[\text{OH}^-]$ makes a large change in pH

Titration of weak acids-strong bases

50.0 mL of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ and add 0.10 M NaOH

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

a) No added NaOH

e) 50 mL (total) NaOH

b) 10 mL of NaOH added

f) 60 mL (total) NaOH

c) 25 mL (total) NaOH

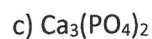
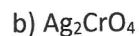
g) 75 mL (total) NaOH

d) 40 mL (total) NaOH

Solubility equilibrium K_{sp}

K_{sp} – solubility constant and is used to predict solubility

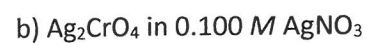
Write the expression for K_{sp} for the following salts



The K_{sp} values for some common ionic solids can be found on page 738. It can also be calculated using the concentration of the salt. Calculate the K_{sp} for the following salts.



The common ion effect also is an issue with solubility as it is with acids and bases. Calculate the solubility of the following salts



K_{sp} and precipitate formation – K_{sp} values can be used to make predictions as to whether or not a precipitate will form when two solutions are mixed.

Q – reaction quotient – Calculated like K_{sp}

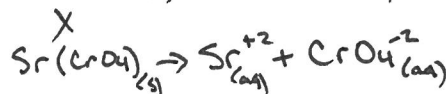
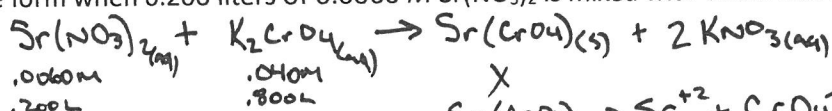
$Q > K_{sp}$ precipitate forms

$Q < K_{sp}$ precipitate does not form

$Q = K_{sp}$ saturated solution

a) Will a precipitate form when 0.0030 M Na_2CrO_4 solution is mixed with a solution of 0.0060 M Sr^{2+} ?

b) Will a precipitate form when 0.200 liters of 0.0060 M $\text{Sr}(\text{NO}_3)_2$ is mixed with 0.800 liters of 0.040 M K_2CrO_4 ?



$$\text{Sr}^{2+}: \frac{.0060\text{M Sr}^{2+}}{1\text{L SOLN}} \times 1.2\text{L} = .0012\text{M Sr}^{2+}$$

$$\text{CrO}_4^{2-}: \frac{.040\text{M CrO}_4^{2-}}{1\text{L SOLN}} \times .8\text{L} = .032\text{M CrO}_4^{2-}$$

$$K_{sp} = [\text{Sr}^{2+}]^1 \cdot [\text{CrO}_4^{2-}]^1 = 3.6 \times 10^{-5} \text{ (From chart)}$$

$$Q = [.0012]^1 \cdot [.032]^1 = 3.8 \times 10^{-5}$$

$Q > K_{sp} \therefore \text{PPT DOES FORM}$

K_{sp} and water solubility

One way to establish equilibrium between a slightly soluble solid and its ions is to stir the solid with water to form a saturated solution. The solubility of the solid, s , in moles/liter is related to the solubility product constant, K_{sp} .

EX 8: BaSO_4

EX 9: Calculate the solubility BaF_2 in

a) moles/liter

b) grams/liter

K_{sp} and the common ion effect

Calculate the solubility of BaSO_4

- a) by itself
- b) when added to $0.10\text{ M Na}_2\text{SO}_4$

Selective precipitation

One way to separate two cations (+) in a water solution is to add an anion (-) that precipitates out one of the cations. This is known as **selective precipitation**.

EX 10: A solution contains Mg^{2+} and Na^+ ions. What is needed to remove the ions from the solution?

EX 11: A solution contains 0.10 M Mg^{2+} ions and 0.10 M Ba^{2+} ions, and you would like to precipitate them by adding CO_3^{2-} ions. Using the following information:
 BaCO_3 ($K_{sp} = 2.6 \times 10^{-9}$) and MgCO_3 ($K_{sp} = 6.8 \times 10^{-6}$), calculate a) which ion will precipitate first and b) in what concentrations.

EX 12: A flask contains a solution of 0.10 M Cl^- and $0.010\text{ M CrO}_4^{2-}$. When AgNO_3 is added:

- a) Which anion, Cl^- or CrO_4^{2-} , will precipitate first?
- b) What percentage of the first anion has been precipitated when the second anion starts to precipitate?