

## Unit V Outline

Part 1 Acid - Base Equilibria, continuedI. COMMON IONA. The Effect of Adding a Common Ion to a Weak Acid/Base Equilibrium

The common-ion effect occurs when an ion that is in a weak acid/base equilibria is added to a equilibrium system.

Consider:  $\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-$

If acetate ion,  $\text{C}_2\text{H}_3\text{O}_2^-$ , is added, according to Le Chantlier's principle there will be a net reaction to the left until equilibrium is reestablished.

If HCl is added, according to Le Chantlier's principle there will be a net reaction to the left until equilibrium is reestablished.

Problems:

1. Calculate the  $[\text{H}_3\text{O}^+]$  for:

a. A 0.10 M acetic acid solution.  $K_a = 1.8 \times 10^{-5}$



*Initial*

*Change*

*at Equilibrium*

b. a 0.10 M acetic acid solution after adding enough  $\text{NaC}_2\text{H}_3\text{O}_2$  to make the solution 0.15 M  $\text{NaC}_2\text{H}_3\text{O}_2$



*Initial*

*Change*

*at Equilibrium*

2. Calculate the pH for a solution that contains 0.015 M  $\text{NH}_3$  (aq) and 0.0050 M  $\text{NH}_4\text{Cl}$ ?  
 $k_b = 1.8 \times 10^{-5}$

*Initial*

*Change*

*at Equilibrium*

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3. Addition of an ion that is not common but does react.  
100.0 mL of 0.2500 M NaOH is added to 250.0 mL of .3500 M  $\text{HClO}_2$   $K_a = 1.1 \times 10^{-2}$   
a. Reaction calculations:

*Moles Before reaction*

*Change*

*Moles After reaction*

*Molarity after reaction*

b. Equilibrium calculations:

*Initial*

*Change*

*at Equilibrium*

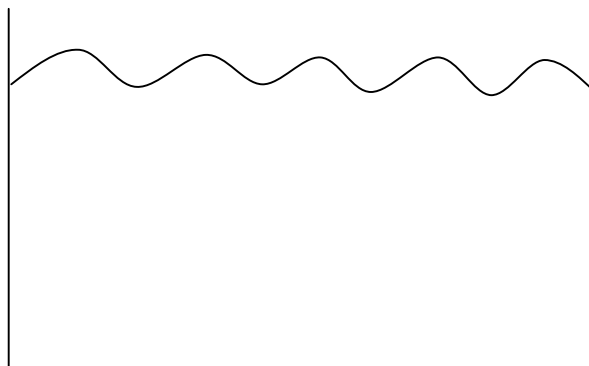


## II. BUFFERS

Buffers are solutions which resist a change in pH when small amounts of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  is added or dilution occurs.

The buffering effect occurs because of the reaction of certain species with the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$

Consider a mixture of  $\text{HC}_2\text{H}_3\text{O}_2 + \text{NaC}_2\text{H}_3\text{O}_2$



## A. Buffering systems:

1. A Weak acid with its salt (a salt that contains the conjugated base of the weak acid)

Example: HClO and NaClO

2. A Weak base with its salt (a salt that contains the conjugated acid of the weak base)

Example: NH<sub>3</sub> and NH<sub>4</sub>Cl

3. Acid Salts

Example: NaHCO<sub>3</sub>

4. A Salt of a weak acid & weak base

Example: NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

**B. Problems:**

(1.) Calculate the  $[H_3O^+]$  for:

a. A solution that is 1.00 M acetic acid and 1.0 M sodium acetate.  $K_a = 1.8 \times 10^{-5}$



*Initial*

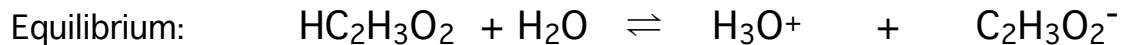
*Change*

*at Equilibrium*

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b. Calculate the pH if 0.01 mole of HCl is added to 1 - Liter of the above buffer solution:

Reaction:



*Initial*

*Change*

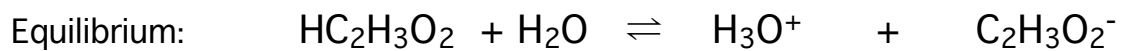
*at Equilibrium*

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c. Calculate the pH if 0.01 mole of KOH is added to a 1-Liter of the buffer solution in

b.

Reaction:



*Initial*

*Change*

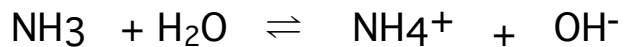
*at Equilibrium*

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d. Calculate the pH if 0.01 mole of KOH is added to 1 Liter of Water

e. Compare the pH of solutions a →d.

- (2.) a. How many moles of  $\text{NH}_4\text{Cl}$  must be added to 1 - Liter of a 0.10 M solution of  $\text{NH}_3(\text{aq})$  to adjust the pH to 9.000.  $K_b = 1.8 \times 10^{-5}$



*Initial*

*Change*

*at Equilibrium*

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- b. Preparation of the above solution

- (3.) a. What concentrations should be used to prepare a cyanic acid-cyanate buffer with a pH of 3.50? .  $K_a = 1.2 \times 10^{-4}$

Equilibrium Eqn:

*Initial*

*Change*

*at Equilibrium*

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- (4.) a. What is the pH of a solution made by mixing 100. mL of 0.15 M HCl and 200. mL of 0.20 M aniline ( $C_6H_5NH_2$ )? Assume that the final volume of the buffer solution is 300. mL.  $K_b = 4.6 \times 10^{-10}$

Reaction:

Moles of HCl =

Moles of Aniline =

Stoichiometry:

Molarity of species after reaction:

Molarity of  $C_6H_5NH_3^+$  =

Molarity of  $C_6H_5NH_2$  =

Equilibrium Eqn:

*Initial*

*Change*

*at Equilibrium*

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(5.) A Strong acid is added to a salt to form a Buffer Solution

- a. How many moles of a strong monoprotic acid must be added to 1-L of a 0.40 M sodium formate,  $\text{NaCO}_2\text{H}$ , solution to prepare a buffer of a  $\text{pH} = 4.35$ .  $K_a = 1.77 \times 10^{-4}$

Reaction:

Equilibrium Eqn:

*Initial*

*Change*

*at Equilibrium*

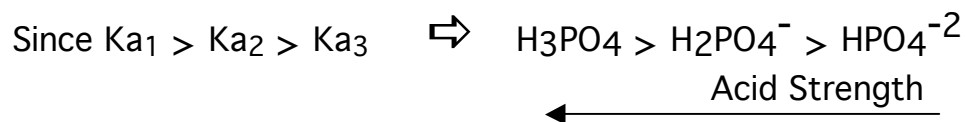
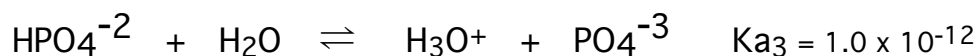
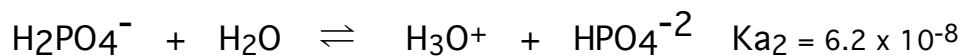
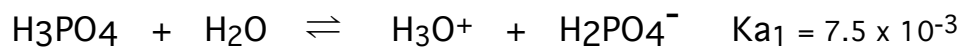
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### III. POLYPROTIC ACIDS

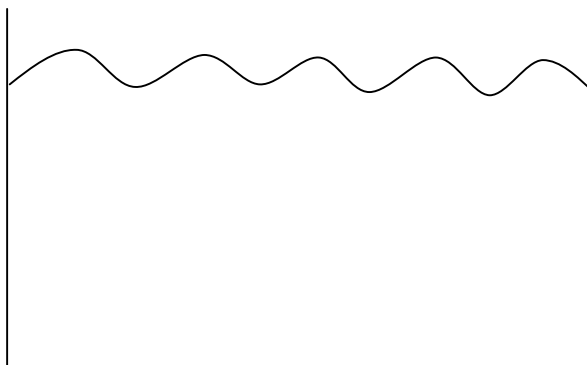
Polyprotic acids are acids which have more than one acidic hydrogen. Polyprotic acids ionize in a stepwise manner. Each step will have a  $K_a$ .

Examples:

Ionization of phosphoric acid



Consider a phosphoric acid solution:

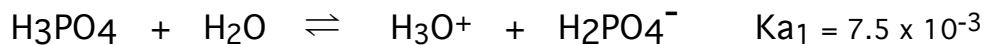


**Problems:**

1. Calculate the  $[H_3O^+]$ ,  $[H_3PO_4]$ ,  $[H_2PO_4^-]$ ,  $[HPO_4^{2-}]$ ,  $[PO_4^{3-}]$  in a 0.10 M solution of phosphoric acid:

The principal source of  $[H_3O^+]$  is the first ionization of  $H_3PO_4$ . The  $H_3O^+$  produced by the 2nd and 3rd ionizations is negligible.

- a. Ionization of  $H_3PO_4$



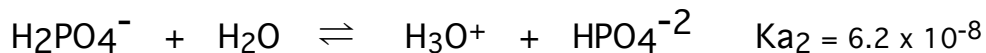
*Initial*

*Change*

*at Equilibrium*

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- b. Ionization of  $H_2PO_4^-$



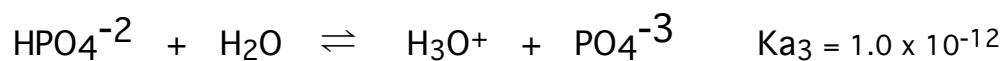
*Initial*

*Change*

*at Equilibrium*

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c. Ionization of  $\text{HPO}_4^{-2}$



*Initial*

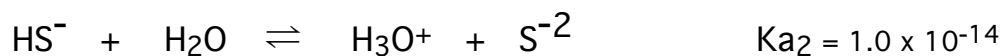
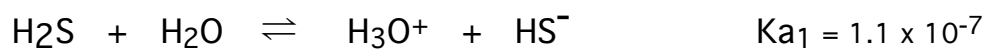
*Change*

*at Equilibrium*

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2. Suppose that we wish the sulfide ion concentration to be  $8.4 \times 10^{-15}$  M in a saturated (0.10 M) solution of  $\text{H}_2\text{S}$ . What hydrogen ion concentration must be maintained by a

buffer to



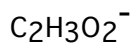
Caution!! The above condensed method can be used only when two of the three equilibrium concentrations are given and we wish to calculate the third.

#### IV. pH OF SALT SOLUTIONS - HYDROLYSIS

Hydrolysis is the reaction of an ion with water to produce either  $\text{H}_3\text{O}^+$  (and a weak base) or  $\text{OH}^-$  (and a weak acid).

Anions derived from weak acids form basic solutions

Examples:



Cations derived from weak bases form acidic solutions

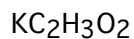
Examples:



##### A. Salts that undergo Hydrolysis:

1. Salt of a Strong Base and Weak Acid will produce basic solutions:

Examples:



2. Salt of a Strong Acid and Weak Base will produce acidic solutions

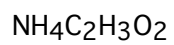
Examples



Hydrolysis of metal ions



3 Salt of a **Weak Acid** and **Weak Base**



4. Salt of a **Strong acid** and a **Strong base**

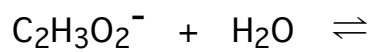


## **B. Problems**

### **1. Salt of a Strong Base and Weak Acid**

Calculate the pH of 0.10 M  $\text{KC}_2\text{H}_3\text{O}_2$ .  $K_a$  for  $\text{HC}_2\text{H}_3\text{O}_2 = 1.8 \times 10^{-5}$

Calculation of  $K_b$



*Initial*

*Change*

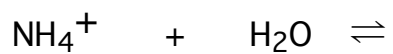
*at Equilibrium*

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2 Salt of a Strong Acid and Weak Base

Calculate the pH of 0.10M  $\text{NH}_4\text{Cl}$ .  $K_b$  for  $\text{NH}_3 = 1.8 \times 10^{-5}$

Calculation of  $K_a$



*Initial*

*Change*

*at Equilibrium*

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3 Salt of a Weak Acid and Weak Base

a.  $\text{NH}_4\text{CN}$   $K_a$  for  $\text{HCN} = 4.0 \times 10^{-10}$   $K_b$  for  $\text{NH}_3 = 1.8 \times 10^{-5}$

b.  $\text{Al}_2(\text{SO}_3)_3$   $K_a$  for  $\text{Al}^{3+} = 1.4 \times 10^{-5}$   $K_{a2}$  for  $\text{HSO}_3^- = 5.6 \times 10^{-8}$

4. Salt of a Strong acid and a Strong base

5. a. Calculate the pH of a solution of 0.10 M  $\text{NaNO}_2$ .  $K_a$  for  $\text{HNO}_2 = 4.5 \times 10^{-4}$

*Initial*

*Change*

*at Equilibrium*

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b. Calculate the percent hydrolysis.

What is the pH of a 0.10 M  $\text{NaHCO}_3$  solution?  $K_{a1} = \text{H}_2\text{CO}_3 = 4.3 \times 10^{-7}$ ,  $K_{a2} = \text{HCO}_3^- = 4.8 \times 10^{-11}$

6. Calculate the pH of a solution if 25.0 mL of .20 M NaOH is added to 50.0 mL of .10 M  $\text{HNO}_2$ .  
 $K_a$  for  $\text{HNO}_2 = 4.5 \times 10^{-4}$

Reaction:

Equilibrium

*Initial*

*Change*

*at Equilibrium*

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7. Calculate the pH of a solution of 0.20 M Na<sub>2</sub>S.  $K_{a2}$  for HS<sup>-</sup> =  $1.0 \times 10^{-14}$

*Initial*

*Change*

*at Equilibrium*

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## V. Titration Curves

A. A Weak Acid is titrated with a strong base

### B. Four Regions

- 1.
- 2.
- 3.
- 4.

50.0 mls of 0.10M HAc is titrated with 0.10 M NaOH

**RXN:** HAc + NaOH → NaAc + H<sub>2</sub>O

**NOTE:** For a weak acid-strong base titration the pH ≠ 7 at the endpoint !

**Region 1 = Before addition of base - WEAK ACID**

**0.00 mL of NaOH added**

pH calculation

**Region 2 = Buffer Region {BEFORE THE EQUIVALENCE POINT}- WEAK ACID**

**25.00 mL of NaOH added**

pH calculation

Method 1

Method 2

**Region 3 = THE EQUIVALENCE POINT- HYDROLYSIS OF A SALT**  
**50.00 mL of NaOH added**

pH calculation

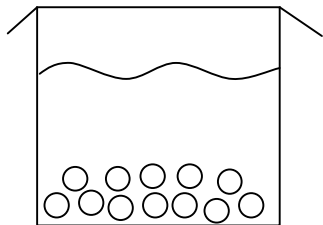
Region 4 = AFTER THE EQUIVALENCE POINT- EXCESS BASE (NaOH)

75.00 mL of NaOH added

pH calculation

## PART 2: SOLUBILITY EQUILIBRIA

In an closed system a solid obtains a dynamic equilibrium with its dissolved state



*Dynamic equilibrium:* rate of dissolving = rate of crystallization (ppt)

If an "insoluble" or "slightly soluble" material is placed in water, an equilibrium is established when the rate of dissolution of ions from the solid equals the rate of precipitation of ions from the *saturated solution*.

### A. Equilibria



### B. Solubility Product constant, K<sub>sp</sub>

### C. Problems

1. At 25°C 0.00188 g of AgCl dissolves in one liter of water. What is the K<sub>sp</sub> of AgCl?

Solubility Limit -

Point where precipitation begins

2. Calculate the solubility of AgBr

3. Calculate the solubility of PbI<sub>2</sub>

4. Calculate the K<sub>sp</sub> for silver chromate if  $s = 6.5 \times 10^{-5}M$

5. How many grams of  $\text{BaF}_2$  will dissolve in 750.0 mls of DI  $\text{H}_2\text{O}$

D. Common Ion Effect on Solubility

Solid is dissolved in a solution containing one of the ions that compose the salt

1. Calculate the solubility of AgCl in 0.1000 M NaCl

2. Calculate the solubility of  $\text{Al}(\text{OH})_3$  at  $\text{pH} = 3.00$

### E. Selective Separation

Separation of ions must lead to minimum contamination of each other.

1.  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  must be separated.  $[\text{Mg}^{2+}] = 0.100 \text{ M}$  and  $[\text{Fe}^{3+}] = 0.100 \text{ M}$

a.  $K_{\text{sp}}$  Equations

b.  $\text{Fe}^{3+}$  calculation

c.  $\text{Mg}^{2+}$  calculations

Will precipitation occur when 50.0 ml of  $\text{Pb}(\text{NO}_3)_2$  solution is added to 50.0 ml of .00200 M KCl? The  $K_{sp}$  of  $\text{PbCl}_2$  is  $1.62 \times 10^{-5}$

Chromate ions are added to a solution in which the original concentration of  $\text{Sr}^{+2}$  is .0010 M. Assuming the concentration of strontium remains the same, at what concentration of chromate ion does a precipitate just start to form?  $K_{sp}$  for  $\text{SrCrO}_4 = 4 \times 10^{-5}$

How many grams of strontium nitrate can be dissolved in 350.0 ml of 0.0100M sodium chromate solution?  $K_{sp}$  for  $\text{SrCrO}_4 = 4 \times 10^{-5}$