EXAM V Material

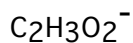## Part 1 Acid – Base Equilibria, continued
Chapter 15
(Page 685-699)

I. **The Acid-Base Properties of Ions and Salts**
 - Hydrolysis

Hydrolysis is the reaction of an ion with water to produce either H_3O^+ (and a weak base) or OH^- (and a weak acid).

Anions derived from weak acids form basic solutions
Examples:

$C_2H_3O_2^-$

NO_2^-

Cations derived from weak bases form acidic solutions
Examples:

NH_4^+

Fe^{3+}

A. Salts that undergo Hydrolysis:

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

Examples:
$KC_2H_3O_2$

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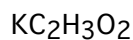
2 Salt of a **Strong Acid** and **Weak Base** will produce acidic solutions

Examples
NH_4Cl

Hydroysis of metal Ions
$AlCl_3$

$FeCl_3$

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

      $NH_4C_2H_3O_2$

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

      NaCl
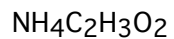
B. Problems

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

    Calculate the pH of 0.10 M $KC_2H_3O_2$. Ka for $HC_2H_3O_2$ = 1.8 x 10^{-5}

    Calculation of Kb

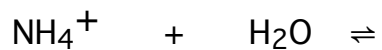$$C_2H_3O_2^- \; + \; H_2O \; \rightleftharpoons$$
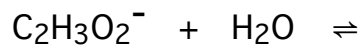
Initial

Change

at Equilibrium

2   Salt of a **Strong Acid** and **Weak Base**

Calculate the pH of 0.10M NH_4Cl. Kb for NH_3 = 1.8 x 10^{-5}

Calculation of Ka

$$NH_4^+ \quad + \quad H_2O \quad \rightleftharpoons$$

Initial

Change

at Equilibrium

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

   a. NH_4CN Ka for HCN = 4.0 x 10^{-10} Kb for NH_3 = 1.8 x 10^{-5}

   b. $Al_2(SO_3)_3$ Ka for Al^{3+} = 1.4 x 10^{-5} Ka_2 for HSO_3^- = 5.6 x 10^{-8}

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

5. a. Calculate the pH of a solution of 0.10 M $NaNO_2$.   Ka for $HNO_2 = 4.5 \times 10^{-4}$

Initial

Change

at Equilibrium

b. Calculate the percent hydrolysis.

6. Calculate the pH of a solution if 25.0 mL of .20 M NaOH is added to 50.0 mL of.10 M HNO_2.   Ka for $HNO_2 = 4.5 \times 10^{-4}$

1st Reaction:
Reaction Eqn:

Before

Change _____

At after rxn

2nd Equilibrium:

Equilibrium Eqn:

Initial

Change _____

at Equilibrium

7. Calculate the pH of a solution of 0.20 M Na_2S. Ka_2 for $HS^- = 1.0 \times 10^{-14}$
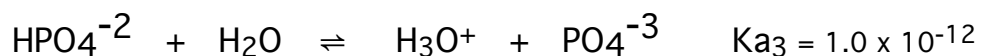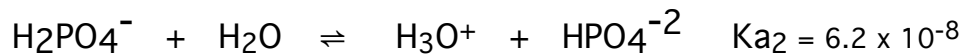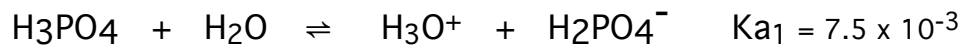
Initial

Change _____

at Equilibrium

II. 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 Ka.

Examples:

Ionization of phosphoric acid

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{-2} \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{-2} + H_2O \rightleftharpoons H_3O^+ + PO_4^{-3} \qquad K_{a3} = 1.0 \times 10^{-12}$$

Since $K_{a1} > K_{a2} > K_{a3}$ ⇨ $H_3PO_4 > H_2PO_4^- > HPO_4^{-2}$

← Acid Strength

Consider a phosphoric acid solution:
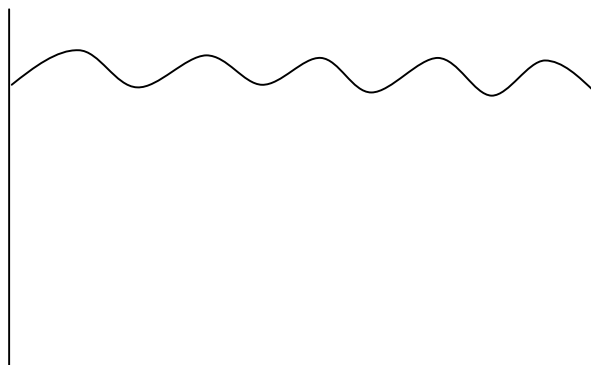
Problems:

1. Calculate the $[H_3O^+]$ and $[H_3PO_4]$ in a 0.10 M solution of phosphoric acid:
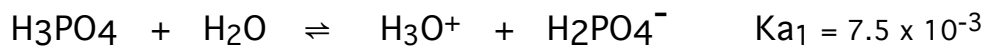   The principal source of $[H_3O^+]$ is the first ionization of H_3PO_4. The H_3O^+ produced by the 2nd and 3rd ionizations is negligible.
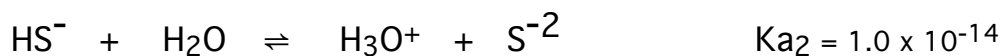
   a. Ionization of H_3PO_4

$$H_3PO_4 \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ H_2PO_4^- \qquad Ka_1 = 7.5 \times 10^{-3}$$

Initial

Change

at Equilibrium

2. Suppose that we wish the sulfide ion concentration to be 8.4×10^{-15} M in a saturated (0.10 M) solution of H_2S. What hydrogen ion concentration must be maintained by a buffer to give this S^{2-} concentration?

$$H_2S \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ HS^- \qquad\qquad Ka_1 = 1.1 \times 10^{-7}$$
$$HS^- \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ S^{-2} \qquad\qquad Ka_2 = 1.0 \times 10^{-14}$$

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.
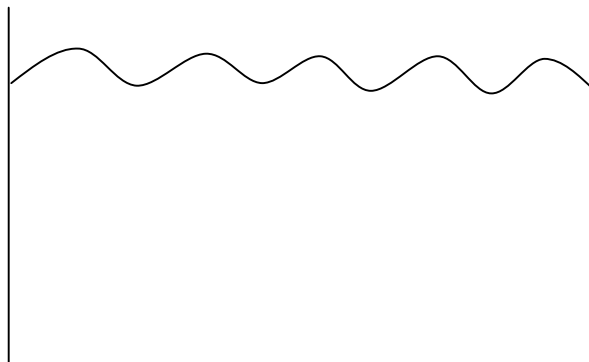
Chapter 16

I. Buffers: Solutions That Resist pH Change

Buffers are solutions which resist a change in pH when small amounts of H_3O^+ or OH^- is added or dilution occurs.

The buffering effect occurs because of the reaction of certain species with the H_3O^+ and OH^-

Consider a mixture of $HC_2H_3O_2$ + $NaC_2H_3O_2$

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)
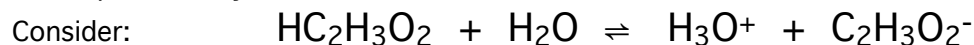   Example: NH_3 and NH_4Cl

3. Acid Salts
    Example: $NaHCO_3$

4. A Salt of a weak acid & weak base
    Example: $NH_4C_2H_3O_2$

II. COMMON ION
A. 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: $HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$

If acetate ion, $C_2H_3O_2^-$, is added, according to Le Chantlier's principle there will be a net reaction to the left until equilibrium is reestablished.
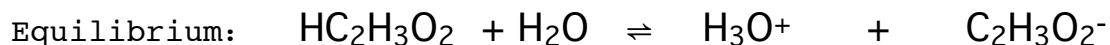
If HCl is added, according to Le Chantlier's principle there will be a net reaction to the left until equilibrium is reestablished.

Problems:

A 0.10 M acetic acid solution after adding enough $NaC_2H_3O_2$ to make the solution 0.15 M $NaC_2H_3O_2$

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

TYPE 1 Calculation:

Equilibrium: $HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$

Initial

Change _____

at Equilibrium

TYPE 2 Calculation:

Henderson – Hasselbalch equation:

Derivation: $Ka = \dfrac{[H^+][A^-]}{[HA]}$

$\log Ka = \log \dfrac{[H^+][A^-]}{[HA]}$

$\log Ka = \log [H^+] + \log \dfrac{[A^-]}{[HA]}$

$- \log [H^+] = -\log Ka + \log \dfrac{[A^-]}{[HA]}$

$\Uparrow$ pH $\Uparrow$ pKa

Therefore: $\quad\quad\quad$ pH $\quad=\quad$ pKa + log $\dfrac{[A^-]}{[HA]}$

1. Calculate the pH for a solution that contains 0.015 M NH_3 (aq) and 0.0050 M NH_4Cl?
   $k_b = 1.8 \times 10^{-5}$

Initial

Change

at Equilibrium

2. 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 $HClO_2$ $K_a = 1.1 \times 10^{-2}$

1st Reaction:

Reaction Eqn:
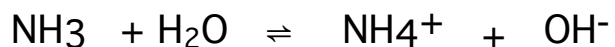
Before

Change

At after rxn

2nd Equilibrium:

Equilibrium Eqn:

Initial

Change

at Equilibrium

3. How many moles of NH_4Cl must be added to 1 - Liter of a 0.10 M solution of $NH_3(aq)$ to adjust the pH to 9.000. $K_b = 1.8 \times 10^{-5}$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Initial

Change _____

at Equilibrium

4. 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 . $K_b = 4.6 \times 10^{-10}$

1st Reaction:

   Reaction Eqn:

Before

Change _____

At after rxn

2nd Equilibrium:

Equilibrium Eqn:

Initial

Change _____

at Equilibrium

5. <u>A Strong acid is added to a salt to form a Buffer Solution</u>
    a. How many moles of a strong monoprotic acid must be added to 1-L of a 0.40 M sodium formate, $NaCO_2H$, solution to prepare a buffer of a pH = 4.35. K_a = 1.77 x 10^{-4}

1st Reaction:
    Reaction Eqn:

Before

Change

At after rxn

2nd Equilibrium:

Equilibrium Eqn:

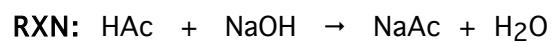*Initial*

Change

at Equilibrium

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_2O

NOTE: For a weak acid-strong base titration the <u>pH ≠ 7</u> at the endpoint !

Region 1 = Before addition of base - WEAK ACID

O.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
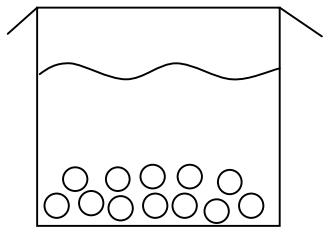## 5O.00 mL of NaOH added

pH calculation

Region 4 = AFTER THE EQUIVALENCE POINT- EXCESS BASE (NaOH)
75.00 mL of NaOH added

pH calculation

Region 3 = THE EQUIVALENCE POINT- HYDROLYSIS OF A SALT

PART 2: SOLUBILITY EQUILIBRIA

In an closed system a solid obtains a <u>dynamic equilibrium</u> 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

$$AgCl\ (s) \ \rightleftharpoons \ Ag^+(aq) \ + \ Cl^-\ (aq)$$
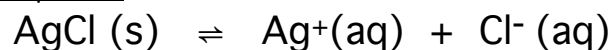
B. Solubility Product constant, Ksp
1.   Ksp of $Fe(OH)_3$ = 4.0 x 10 $^{-38}$ & Ksp of $Al(OH)_3$ = 1.6 x 10 $^{-32}$

2. Solubility, s   (as Molar solubility)
   a. AgCl

   b. Ag_2S

2.   Solutilbity Limit

Point where precipitation begins

C. Problems

    1. At 25°C 0.00188 g of AgCl dissolves in one liter of water. What is the Ksp of AgCl?

    2. Calculate the solubility of $AgIO_3$ Ksp of $AgIO_3$ = 3.0 x 10^{-8}

    3. Calculate the solubility of $HgBr_2$ Ksp of $HgBr_2$ = 1.3 x 10^{-19}

    4. Calculate the Ksp for silver chromate if s = 6.5 x $10^{-5}M$

    5. How many grams of $Ba(IO_3)_2$ will dissolve in 750.0 mls of DI H_2O Ksp of $Ba(IO_3)_2$ = 1.57 x 10^{-9}

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 $Al(OH)_3$ at pH = 3.00

   3. Calculate the solubility of ZnS in a saturated H_2S solution (o.10 M) at a pH = 6.00

E. <u>Selective Separation</u>

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

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

    a. K_{sp} Equations

    b. Fe^{3+} calculation

    c. Mg^{2+} calculations