MNHS AP Chemistry

## Section 15.1 Solutions of Acids or Bases Containing a Common Ion

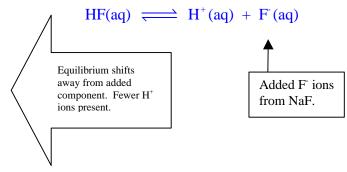
<u>Common ion</u> the presence of an ion which appears in both the acid (or base) and a salt in solution.

- <u>Common ion effect</u> the shift in equilibrium position that occurs because of the addition of an ion already involved in the equilibrium reaction.
  - For example if a solution of NaF and HF are mixed together, F<sup>-</sup> would be the common ion. If we look at the dissociation of each compound:

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NaF(s) \xrightarrow{H_2O(l)} Na<sup>+</sup>(aq) + F<sup>-</sup>(aq)
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 $HF(aq) \implies H^+(aq) + F^-(aq)$ 

According to Le Châtelier's principle, an increase in concentration of an ion will shift the equilibrium away from the ion added.



This makes the solution less acidic than a solution of HF alone.

## Section 15.2 Buffered Solutions

<u>Buffered solution</u> - a solution that resists a change in its pH when either hydroxide ions or protons (hydrogen ions) are added. A buffered solution is composed of a weak acid and its salt.

Buffered solutions are simply solutions of weak acids or bases containing a common ion. The pH calculations on buffered solutions require exactly the same procedures introduced in Chapter 14.

When a strong acid or base is added to a buffered solution, it is best to deal with the stoichiometry of the resulting reaction first. After the stoichiometric calculations are completed, then consider the equilibrium calculations.

How does a buffer work?

Suppose in a buffered solution we have large amounts of a weak acid HA and its conjugate base A<sup>-</sup>.

1. If OH<sup>-</sup> ions are added to this system (the reaction will proceed in the forward direction)

### $HA + OH^{-} \rightarrow A^{-} + H_2O$

The net result is that OH<sup>-</sup> ions are not allowed to accumulate but are replaced by A<sup>-</sup> ions. So pH changes only slightly.

2. If H<sup>+</sup> ions are added to this system (the reaction will proceed in the reverse direction)

## $H^+ + A^- \rightarrow HA$

The net result is that  $H^{\dagger}$  ions are not allowed to accumulate but are replaced by HA molecules. So pH changes only slightly.

\*\*Notes have been derived from Zumdahl 4<sup>th</sup> ed. - All page and table references are made to this edition.

#### MNHS AP Chemistry

Thus the stability of the pH under these conditions can be understood by examining the equilibrium expression for the dissociation of HA:

$$\mathbf{K}_{a} = \frac{\left[\mathbf{H}^{+}\right]\left[\mathbf{A}^{-}\right]}{\left[\mathbf{H}\mathbf{A}\right]}$$

Rearrange:

$$\left[\mathbf{H}^{+}\right] = \mathbf{K}_{a} \frac{\left[\mathbf{H}\mathbf{A}\right]}{\left[\mathbf{A}^{+}\right]}$$

in other words the equilibrium concentration of  $H^+$ , and thus pH, is determined by the ratio [HA]/[A<sup>-</sup>]. If the amounts of HA and A<sup>-</sup> are very large to start with compared to the amount of  $H^+$  (or OH<sup>-</sup>) ions added, the change in the [HA]/[A<sup>-</sup>] will be small.

What if the buffered solution is made from a weak base and the salt of the conjugate acid?

1. If H<sup>+</sup> ions are added to this system (the reaction will proceed in the forward direction)

 $B + H^{+} \rightarrow BH^{+}$ 

2. If OH<sup>-</sup> ions are added to this system (the reaction will proceed in the reverse direction)

 $BH^+ + OH^- \rightarrow B + H_2O$ 

<u>Henderson-Hasselbalch equation</u> - Using the above relationship, if we were to take the log form of the K<sub>a</sub> expression we would get an equation which is useful for calculating the pH of solutions when the [HA]/[A<sup>-</sup>] is known.

$$pH = pK_a + log\left(\frac{\left[A^{*}\right]}{\left[HA\right]}\right) = pK_a + log\left(\frac{\left[base\right]}{\left[acid\right]}\right)$$

For a particular buffering system (acid-conjugate base pair), all solutions that have the same ratio [A<sup>-</sup>]/[HA] will have the same pH. See p. 720 (purple box) for a summary of buffered solutions.

#### Section 15.3 Buffer Capacity

<u>Buffer capacity</u> - represents the amount of protons (hydrogen ions) or hydroxide ions the buffer can absorb without a significant change in pH. The capacity of a buffered solution is determined by the magnitudes of [HA] and [A<sup>-</sup>].

#### Section 15.4 Titrations and pH Curves

<u>pH curve (titration curve)</u> -the progress of an acid-base titration monitored by plotting the pH of the solution being analyzed as a function of the amount of titrant added.

<u>Millimole</u> - since most titrations involve very small quantities, the mole is inconveniently large. Since most volumes will be measured in milliliters, it would also be convenient to measure moles in a quantity equal to a thousandth of a mole.

Molarity = 
$$\frac{\text{mol solute}}{\text{L solution}} = \frac{\frac{\text{mol solute}}{1000}}{\frac{\text{L solution}}{1000}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

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## MNHS AP Chemistry

- Strong Acid-Strong Base titration: Since both the acid and base are strong, each will dissociate completely. It is thus important to determine the number of moles of H<sup>+</sup> and OH<sup>-</sup> produced. Three situations could occur:
  - If you have equal moles of H<sup>+</sup> and OH<sup>-</sup>, they will cancel each other out and you will be left with a neutral solution.
  - 2. If you have more H<sup>+</sup> ions than OH<sup>-</sup> ions, the extra H<sup>+</sup> will make the solution acidic (the other H<sup>+</sup> ions will combine with the OH<sup>-</sup> ions to make water).
  - 3. If you have more OH<sup>-</sup> ions than H<sup>+</sup> ions, the extra OH<sup>-</sup> will make the solution basic (alkaline) (the other OH<sup>-</sup> ions will combine with the H<sup>+</sup> ions to make water).

Stoichiometric point (or equivalence point): the point in the titration where an amount of base has been added to exactly react with all the acid originally present.

<u>Weak acid-Strong base titration</u>: This type of titration problem actually has two components, the stoichiometry of the reaction and the equilibrium which will occur. Each should be dealt with separately.

- 1. The stoichiometry the reaction of hydroxide ion with the weak acid is assumed to run to completion, and the concentrations of the acid remaining and conjugate base formed are determined.
- 2. The equilibrium the position of the weak acid equilibrium is determined, and the pH is calculated.

The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.

<u>Weak Base-Strong acid titration</u>: See instructions for weak acid-strong base titrations above.

The pH at the equivalence point of a titration of a weak base with a strong acid is always less than 7.

#### Section 15.5 Acid-Base Indicators

<u>Acid-base indicator</u>: marks the end point of a titration by changing color. It is important to note that the end point is defined by the change in color of the indicator. The equivalence point is defined by the reaction stoichiometry.

See figure 15.8 on page 744

## Section 15.6 Solubility Equilibria and the Solubility Product

<u>Solubility product constant (solubility product)</u>: K<sub>sp</sub> - expresses the equilibrium position that occurs for the solubility of solids. It also expresses at what point solution would be considered to be saturated.

For the following reaction:

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AB(s) \rightarrow nA^{+}(aq) + mB^{-}(aq)
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So the equilibrium expression would be:

 $K_{sp} = [A^{+}]^{n}[B^{-}]^{m}$ 

## Section 15.7 Precipitation and Qualitative Analysis

<u>Ion Product</u>: (Q) just like the expression for K<sub>sp</sub> for a given solid expect that initial concentrations are used instead of equilibrium concentrations.

If Q is greater than  $K_{sp}$ , precipitation occurs and will continue until the concentrations are reduced to the point that they satisfy  $K_{sp}$ .

If Q is less than  $K_{sp}$ , no precipitation occurs.

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<u>Selective precipitation</u>: uses a reagent whose anion forms a precipitate with only one or a few of the metal ions in a mixture.

# Section 15.8 Equilibria Involving Complex Ions

Read through this section and make yourself familiar with it.