- Chapter 17
  Additional Aspects of Aqueous Equilibria

- This chapter deals with the solution equilibrium when it contain more than one solute.

- The Common-Ion Effect

- Consider a solution of acetic acid:

- The Common-Ion Effect

- Consider a solution of acetic acid:

- If acetate ion is added to the solution, Le Châtelier says the equilibrium will shift to the left.

- The Common-Ion Effect

"The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte."

- The Common-Ion Effect

Calculate the fluoride ion concentration and pH of a solution that is 0.20 *M* in HF and 0.10 *M* in HCl. K_a for HF is 6.8×10^{-4}.

- The Common-Ion Effect

- The Common-Ion Effect

= x

$1.4 \times 10^{-3} = x$

- The Common-Ion Effect

- Therefore, $[F^-] = x = 1.4 \times 10^{-3}$

$[H_3O^+] = 0.10 + x = 0.10 + 1.4 \times 10^{-3} = 0.10\ M$

- So, pH = −log (0.10)

  pH = 1.00

So you see that when a strong acid is mixed with a weak acid the pH is fully because of the strong acid.

PRACTICE EXERCISE Page 723

Calculate the pH of a solution containing 0.085 *M* nitrous acid (HNO_2; $K_a = 4.5 \times 10^{-4}$) and

0.10 *M* potassium nitrite (KNO_2)

Home work question, show all work and draw the table.

- ***Answer:*** 3.42
- Buffers:
- Solutions of a weak conjugate acid-base pair.
- They are particularly resistant to pH changes, even when strong acid or base is added.
- The buffer solutions are made of a weak acid or weak base and the salt of that acid or base.

Examples:

acetic acid and sodium acetate

ammonia and ammonium acetate

- Buffers

If a small amount of hydroxide is added to an equimolar solution of HF in NaF, for example, the HF reacts with the OH^- to make F^- and water.

- Buffers

If acid is added, the F^- reacts to form HF

- Buffer Calculations

Consider the equilibrium constant expression for the dissociation of a generic acid, HA:

- Buffer Calculations

Rearranging slightly, this becomes

- Buffer Calculations
- So
- Henderson–Hasselbalch Equation

What is the pH of a buffer that is 0.12 *M* in lactic acid, $HC_3H_5O_3$, and 0.10 *M* in sodium lactate? K_a for lactic acid is

1.4×10^{-4}.

- Henderson–Hasselbalch Equation
- **PRACTICE EXERCISE**

- Calculate the pH of a buffer composed of 0.12 *M* benzoic acid and 0.20 *M* sodium benzoate.
- Ka = 6.3x 10^{-5}
- ***Answer:*** 4.42

Now we know the molarity we can calculate the moles.

(2.0L) (0.18M) = 0.36 moles of NH_4^+

- Buffer Capacity and pH range
- The pH range is the range of pH values over which a buffer system works effectively.

Since

- *If the concentration of the weak acid and its conjugate base is the same,*

$$pH = pK_a$$

- It is best to choose an acid with a pKa close to the desired pH.
- Buffers usually have a usable range within +/- 1 pH unit of pKa
- Buffering Capacity

The buffering capacity is the amount of acid or base that a base can neutralize before the pH begins to change.

A 1L solution that is 1M with respect to $HC_2H_3O_2$ and 1M with respect to Na $C_2H_3O_2$ has the same $[H^+]$ as 0.1M concentration of both the components.

BUT…………

The buffering capacity of the first solution is going to be much more than the second as it has a higher concentration.

The greater the amounts of the conjugate acid base pair, the more resistant the ratio of their concentration and therefore the pH is to change.

- When Strong Acids or Bases Are Added to a Buffer…

…it is safe to assume that all of the strong acid or base is consumed in the reaction.

- Addition of Strong Acid
  or Base to a Buffer

1. Determine how the neutralization reaction affects the amounts of the weak acid and its conjugate base in solution.
2. Use the Henderson–Hasselbalch equation to determine the new pH of the solution.

- Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol $HC_2H_3O_2$ and 0.300 mol $NaC_2H_3O_2$ to enough water to make 1.00 L of solution. The pH of the buffer is 4.74. Calculate the pH of this solution after 0.020 mol of NaOH is added.

Before the reaction, since

mol $HC_2H_3O_2$ = mol $C_2H_3O_2^-$

pH = pKa + 0

pH = pK_a = 4.74

- Calculating pH Changes in Buffers
- Calculating pH Changes in Buffers
- Addition of Strong Acid or Base to a Buffer

1. Determine how the neutralization reaction affects the amounts of the weak acid and its conjugate base in solution.
2. Use the Henderson–Hasselbalch equation to determine the new pH of the solution.

- NOW…..

let us determine the pH of the solution if the same 0.020 M NaOH is addes to the to the same volume of water.

pOH of the base = - log [OH-]

= - log [0.020]

= 1.6989

pH = 14 - 1.6989 = 12.3

- I need the home work in the next five minutes….. And not after that.
- Titration

A known concentration of base (or acid) is slowly added to a solution of acid (or base).

- Titration

A pH meter or indicators are used to determine when the solution has reached the equivalence point, at which the stoichiometric amount of acid equals that of base.

- Strong acid strong base
- Weak acid with a strong base
- Strong acid weak base
- Weak acid and weak base
- Titration of a Strong Acid with a Strong Base

From the start of the titration to near the equivalence point, the pH goes up slowly.

- Titration of a Strong Acid with a Strong Base

Just before and after the equivalence point, the pH increases rapidly.

- Titration of a Strong Acid with a Strong Base

At the equivalence point, moles acid = moles base, and the solution contains only water and the salt from the cation of the base and the anion of the acid.

- Titration of a Strong Acid with a Strong Base

The cation of the strong base and the anion of the strong acid have no effect on the pH.

- Titration of a Strong Acid with a Strong Base

As more base is added, the increase in pH again levels off.

- You *are* familiar with this titration

Can you remember?

- What would a curve when the strong base is titrated against a strong acid look like?
- 17.6
- Calculate the pH when the following quantities of 0.100 *M* NaOH solution have been added to 50.0 mL of 0.100 *M* HCl solution: **(a)** 49.0 mL, **(b)** 51.0 mL.

1. Find the number of moles of HCl

The number of moles of H^+ in the original HCl solution is given by the product of the volume of the solution (50.0 mL = 0.0500 L) and its molarity (0.100 *M*):

- a. Likewise, the number of moles of OH^- in 49.0 mL of 0.100 *M* NaOH is
- Now write the reaction and write the moles of the respective components:

Now find the molarity of H+ ion as we need to know that in order to calculate the pH

-
- Titration of a Weak Acid with a Strong Base
- The pH of the acid by itself will depend on the percent dissociation.
- Unlike in the previous case, the conjugate base of the acid affects the pH when it is formed, so we need to treat the product as a buffer solution.
- The pH at the equivalence point will be >7.
- Phenolphthalein is commonly used as an indicator in these titrations because its color change is between pH 8.5 and 10.
- Titration of a Weak Acid with a Strong Base

At each point below the equivalence point, the pH of the solution during titration is determined from the amounts of the acid and its conjugate base present at that particular time.

- Titration of a Weak Acid with a Strong Base

With weaker acids, the initial pH is higher and pH changes near the equivalence point are more subtle.

- Titration of a Weak Base with a Strong Acid
- The pH at the equivalence point in these titrations is < 7.
- Methyl red is the indicator of choice as its color change is between 4.2 and 6.0
- What will happen when we have a weak acid and weak base titration:

What will happen when we have a weak acid and weak base titration:

1. An anion that is the conjugate base of a weak acid will increase the pH.
2. A cation that is the conjugate acid of a weak base will decrease the pH.

- **Titration curves for weak acid vs weak base**
- The common example of this would be acetic acid and ammonia.

$CH_3COOH + NH_3 \rightarrow CH_3COO^- + NH_4^+$

- It so happens that these two are both about equally weak - in that case, the equivalence point is approximately pH 7.
- Notice that there isn't any steep bit on this graph. Instead, there is just what is known as a "point of inflexion". That lack of a steep bit means that it is difficult to do a titration of a weak acid against a weak base

- Titrations of Polyprotic Acids

  In these cases there is an equivalence point for each dissociation.

- Now you will plug it into the
- Kb = ………………….
- Equation and it will give you the [OH]

Concentration with which you will calculate the pOH. Then to get pH……….

- We end here……..
- Solubility Products

Consider the equilibrium that exists in a saturated solution of $BaSO_4$ in water:

- Solubility Products

The equilibrium constant expression for this equilibrium is

$K_{sp} = [Ba^{2+}] [SO_4^{2-}]$

where the equilibrium constant, K_{sp}, is called the solubility product.

- Solubility Products
- K_{sp} is *not* the same as solubility.
- Solubility is generally expressed as the mass of solute dissolved in 1 L (g/L) or 100 mL (g/mL) of solution, or in mol/L (*M*).
- Factors Affecting Solubility

- The Common-Ion Effect
  - If one of the ions in a solution equilibrium is already dissolved in the solution, the equilibrium will shift to the left and the solubility of the salt will decrease.
- Factors Affecting Solubility
- pH
  - If a substance has a basic anion, it will be more soluble in an acidic solution.
  - Substances with acidic cations are more soluble in basic solutions.
- Factors Affecting Solubility
- Complex Ions
  - Metal ions can act as Lewis acids and form complex ions with Lewis bases in the solvent.
- Factors Affecting Solubility
- Complex Ions
  - The formation of these complex ions increases the solubility of these salts.
- Factors Affecting Solubility
- Amphoterism
  - Amphoteric metal oxides and hydroxides are soluble in strong acid or base, because they can act either as acids or bases.
  - Examples of such cations are Al^{3+}, Zn^{2+}, and Sn^{2+}.
- Will a Precipitate Form?
- In a solution,
  - If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.
  - If $Q < K_{sp}$, more solid will dissolve until $Q = K_{sp}$.
  - If $Q > K_{sp}$, the salt will precipitate until $Q = K_{sp}$.
- Selective Precipitation of Ions

  One can use differences in solubilities of salts to separate ions in a mixture.