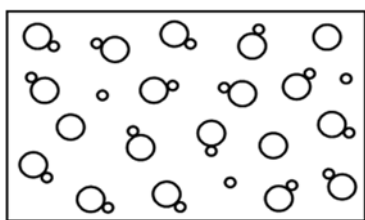


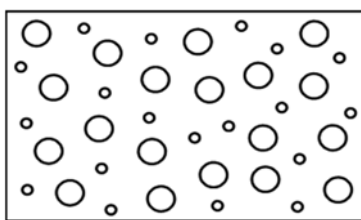
## Study Guide for Acid-Base Chemistry, Buffers, Titrations, and $K_{sp}$

- In a Brønsted-Lowry acid-base reaction, the  $H^+$  is transferred from the acid to the base. General examples of an acid (HA) or a base (B) reacting with water include the following.
  - $HA + H_2O \rightleftharpoons H_3O^+ + A^-$
  - $B + H_2O \rightleftharpoons HB^+ + OH^-$
- Examples of Brønsted-Lowry acid-base pairs include the following.
  - HA (acid) and  $A^-$  (base)
  - $HB^+$  (acid) and B (base)
  - $H_2O$  (acid) and  $OH^-$  (base)
  - $H_3O^+$  (acid) and  $H_2O$  (base)
- Memorize the six strong acids: HCl, HBr, HI,  $HNO_3$ ,  $HClO_4$ , and  $H_2SO_4$
- Examples of weak acids: HOCl,  $HClO_2$ , HF,  $H_2CO_3$ ,  $H_3PO_4$ ,  $HC_2H_3O_2$  (also written as  $CH_3COOH$ )
- Examples of strong bases: LiOH, NaOH, KOH,  $Ca(OH)_2$ ,  $Sr(OH)_2$ ,  $Ba(OH)_2$
- Examples of weak bases:
  - An amine is a molecule that is structurally similar to  $NH_3$ . It contains a nitrogen atom that acts as a  $H^+$  acceptor. Examples of amines include  $CH_3NH_2$ ,  $CH_3CH_2NH_2$ ,  $(CH_3)_3N$ , and  $C_5H_5N$ .
  - An anion that represents the conjugate base of a weak acid acts as a  $H^+$  acceptor. Examples of these anions include  $F^-$ ,  $NO_2^-$ ,  $CN^-$ ,  $ClO^-$ ,  $ClO_2^-$ ,  $CO_3^{2-}$ , and  $PO_4^{3-}$ .
- Be familiar with the following equations and how they are used to solve problems.
  - $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$  @ 25°C
  - $K_w = K_a \times K_b$
  - $pH = -\log[H^+]$
  - $pOH = -\log[OH^-]$
  - $pK_a = -\log K_a$
  - $pK_b = -\log K_b$
  - $pH = pK_a + \log \frac{[A^-]}{[HA]}$

- If you are given a particle diagram, a weak acid and a strong acid could be represented like this:



weak acid (partially dissociated)



strong acid (100% dissociated)

- In a solution of a weak acid, the weak acid molecule (HA) is only partially ionized in solution. Therefore the species that is present in the highest concentration is the HA itself, as opposed to ions such as  $H^+$  (or  $H_3O^+$ ),  $OH^-$ , or  $A^-$ .
- A strong acid undergoes dissociation (or ionization) or reacts with water as follows.  
 $HNO_3 \rightarrow H^+ + NO_3^-$  or  $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$
- A strong base undergoes dissociation in water as follows.  
 $KOH \rightarrow K^+ + OH^-$
- A strong acid reacts with a strong base as follows.  
 $H^+ + OH^- \rightarrow H_2O$  or  $H_3O^+ + OH^- \rightarrow 2 H_2O$
- A weak acid (HA) undergoes dissociation (or ionization) or reacts with water as follows.  
 $HA \rightleftharpoons H^+ + A^-$  or  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

The  $K_a$  expression for a weak acid is written as follows.

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- A weak base (B or  $A^-$ ) reacts with water as follows.  
 $B + H_2O \rightleftharpoons HB^+ + OH^-$  or  $A^- + H_2O \rightleftharpoons HA + OH^-$

The  $K_b$  expression is written as follows.

$$K_b = \frac{[HB^+][OH^-]}{[B]} \quad \text{or} \quad K_b = \frac{[HA][OH^-]}{[A^-]}$$

- The equation for the percent ionization of an acid (or a base) is shown below. When comparing two different acids that have the same value of  $[HA]$ ,
  - the acid with the greater value for % ionization is the stronger acid (with a larger  $K_a$ )
  - the acid with the greater  $K_a$  value has the greater value for % ionization

$$\text{percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HA]_{\text{initial}}} \times 100\%$$

$$\text{percent ionization} = \frac{[OH^-]_{\text{equilibrium}}}{[B]_{\text{initial}}} \times 100\%$$

- If you are given [HA] and the pH of the solution, you can calculate  $K_a$ .

Example: The pH of 0.10 M HX is 3.00. Calculate the value of  $K_a$  for HX.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(10^{-3})(10^{-3})}{(0.10 - 10^{-3})} = \frac{10^{-6}}{0.099} = 1.0 \times 10^{-5}$$

- If you are given [HA] and the  $K_a$  value, you can calculate the pH of the solution.

Example: The  $K_a$  for HX is  $1.0 \times 10^{-8}$ . Calculate the pH of 0.50 M HX.

The quadratic equation is not required on the AP Exam. If you need to solve for  $x$  in a weak acid problem similar to the one shown below, make the simplifying assumption that  $x$  is much less than [HA].

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{(0.50 - x)} = \frac{(x)(x)}{(0.50)} = 1.0 \times 10^{-8}$$

$$x^2 = 5.0 \times 10^{-9}$$

$$x = [\text{H}^+] = \sqrt{5.0 \times 10^{-9}} = 7.1 \times 10^{-5} \text{ M (which is much less than 0.50 M)}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(7.1 \times 10^{-5}) = 4.15$$

- When comparing two different weak acids,
  - the acid that has the greater value for  $K_a$  is the stronger acid
  - if each solution has the same [HA], the solution with the lower pH value is the stronger acid
  - if each solution has the same pH value, the solution with the smaller [HA] is the stronger acid
  - if HX has a greater  $K_a$  than HY, then  $\text{Y}^-$  has a greater  $K_b$  than  $\text{X}^-$
- Consider the following reaction:  $\text{HX} + \text{Y}^- \rightleftharpoons \text{HY} + \text{X}^-$ 
  - If  $K > 1$  (product-favored), then HX is the stronger acid and  $\text{Y}^-$  is the stronger base
  - If  $K < 1$  (reactant-favored), then HY is the stronger acid and  $\text{X}^-$  is the stronger base

Concentration of $\text{HC}_2\text{H}_3\text{O}_2$	$[\text{H}^+]$	pH	% ionization
0.10 M	0.0013 M	2.89	1.3%
0.010 M	$4.2 \times 10^{-4} \text{ M}$	3.38	4.2%
0.0010 M	$1.3 \times 10^{-4} \text{ M}$	3.89	13%

- Suppose you have a solution of a weak acid HA. Dilution of a system such as this, which is described by the reaction equilibrium  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$  decreases the concentrations of all three species, HA,  $\text{H}^+$ , and  $\text{A}^-$ . Dilution causes the value of  $Q$  to become less than  $K_a$ . When  $Q < K$ , the equilibrium position shifts towards the products. This can also be understood by saying that, since the concentrations of all three species have been decreased, the equilibrium position shifts in such a way as to increase the concentration of the aqueous particles. Shifting to the right side of the equation makes sense since there are more moles of aqueous particles on the right side of the equation (2 vs. 1). Therefore when a weak acid is diluted, the % ionization will increase.

- If you have a polyprotic acid such as  $\text{H}_2\text{CO}_3$  or  $\text{H}_3\text{PO}_4$ , the 1<sup>st</sup> ionization step has a larger  $K_a$  value than the 2<sup>nd</sup> ionization step. In other words  $K_{a1} > K_{a2}$ . Why? Because it is easier to remove the  $\text{H}^+$  ion from a neutral molecule than it is to remove the  $\text{H}^+$  ion from a negatively charged ion. This can be explained because the negative ion ( $\text{HX}^-$ ) has a greater attraction for the  $\text{H}^+$  ion than the neutral molecule ( $\text{H}_2\text{X}$ ). If there is a 3<sup>rd</sup> ionization step, then  $K_{a2} > K_{a3}$ .
- If you know the  $K_a$  of a weak acid ( $\text{HA}$  or  $\text{HB}^+$ ), you can calculate the  $K_b$  for the conjugate base ( $\text{A}^-$  or  $\text{B}$ ).
  - $K_a \times K_b = K_w = 1.0 \times 10^{-14}$
  - Example: The  $K_a$  for acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) is  $1.8 \times 10^{-5}$ . Calculate the  $K_b$  for the acetate ion ( $\text{C}_2\text{H}_3\text{O}_2^-$ ).

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

- If you know the  $K_b$  of a weak base ( $\text{B}$  or  $\text{A}^-$ ), you can calculate the  $K_a$  for the conjugate acid ( $\text{HB}^+$  or  $\text{HA}$ ).
  - $K_a \times K_b = K_w = 1.0 \times 10^{-14}$
  - Example: The  $K_b$  for the carbonate ion ( $\text{CO}_3^{2-}$ ) is  $1.8 \times 10^{-4}$ . Calculate the  $K_a$  for the hydrogen carbonate ion ( $\text{HCO}_3^-$ ).

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

- If you are given the concentration of a weak base and the pH of the solution, you can calculate  $K_b$ .

Example: The pH of 0.10 M  $\text{NH}_3$  is 11.13. Calculate the value of  $K_b$  for  $\text{NH}_3$ .

If the pH = 11.13, then the pOH = 14.00 – 11.13 = 2.87

$$[\text{OH}^-] = 10^{-2.87} = 0.0013 \text{ M}$$

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{(0.0013)(0.0013)}{(0.10 - 0.0013)} = 1.7 \times 10^{-5}$$

- If you are given  $K_b$  and the concentration of a weak base, you can calculate the pH of the solution.

Example: The  $K_b$  for  $\text{OCl}^-$  is  $3.3 \times 10^{-7}$ . Calculate the pH of 0.50 M  $\text{NaOCl}$ .

Note that the quadratic equation is not necessary on the AP Exam. If you need to solve for  $x$  in a problem similar to the one shown below, make the simplifying assumption that  $x$  is much less than the concentration of the base.

$$K_b = \frac{[\text{OH}^-][\text{HOCl}]}{[\text{OCl}^-]} = \frac{(x)(x)}{(0.50 - x)} = \frac{(x)(x)}{(0.50)} = 3.3 \times 10^{-7}$$

$$x^2 = 1.65 \times 10^{-7}$$

$$x = [\text{OH}^-] = \sqrt{1.65 \times 10^{-7}} = 4.1 \times 10^{-4} \text{ M} \text{ (which is much less than 0.50 M)}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.1 \times 10^{-4}) = 3.39$$

$$\text{pH} = 14.00 - 3.39 = 10.61$$

- The Effect of Temperature on the pH of Pure Water



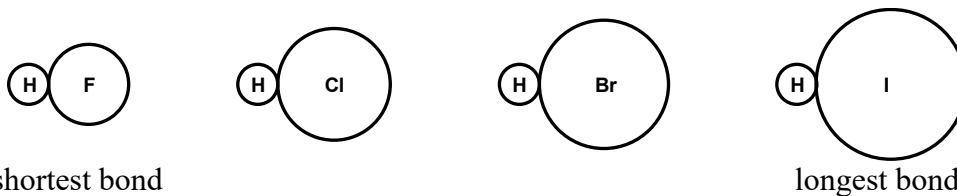
The auto-ionization of water is represented by the equation above. Values of  $pK_w$  at various temperatures are listed in the table below.

Temperature (°C)	$pK_w$
0	14.9
10	14.5
20	14.2
30	13.8
40	13.5

The data represented in the table above helps to show that the auto-ionization of water is an endothermic process.

- If the temperature is equal to 25°C,
    - $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  and  $pK_w = 14.00$
    - The pH of pure water = 7.00 and the pOH of pure water = 7.00
  - If the temperature is less than 25°C, the reaction has shifted toward the left (reactants).
    - $K_w = [\text{H}^+][\text{OH}^-]$  is less than  $1.0 \times 10^{-14}$  and  $pK_w$  is greater than 14.00
    - the pH of pure water > 7.00 and the pOH of pure water > 7.00
  - If the temperature is greater than 25°C, the reaction has shifted toward the right (products).
    - $K_w = [\text{H}^+][\text{OH}^-]$  is greater than  $1.0 \times 10^{-14}$  and  $pK_w$  is less than 14.00
    - the pH of pure water < 7.00 and the pOH of pure water < 7.00
- Salts can be classified as acidic, basic, or neutral.
    - Group 1 cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ...) and heavier group 2 cations ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) are neutral.
    - Anions that represent the conjugate base of a strong acid are neutral (e.g.  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$ )
    - Cations that represent the conjugate acid of a weak base are acidic (e.g.  $\text{NH}_4^+$ ,  $\text{CH}_3\text{NH}_3^+$ )  
Example:  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
    - Anions that represent the conjugate base of a weak acid are basic (e.g.  $\text{F}^-$ ,  $\text{NO}_2^-$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ )  
Example:  $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$

- Periodic trends can be used to explain the relative strength of acids.
  - Within a group, relative acid strength can be predicted based on bond energies.
  - The atomic radius trend for the halogens is as follows.  $F < Cl < Br < I$
  - The relative bond length for HX molecules is as follows.



- Bond strength for the H–X bond is as follows.  
 $HF (567 \text{ kJ/mol}) > HCl (431 \text{ kJ/mol}) > HBr (366 \text{ kJ/mol}) > HI (299 \text{ kJ/mol})$
- Acid strength increases as the strength of the H–X bond decreases. Weaker bonds are easier to break. HF is the weakest acid in this series, and HI is the strongest acid in this series.
- Within a period, relative acid strength can be predicted based on electronegativity values and bond polarity. HF is a stronger acid than H<sub>2</sub>O because F is more electronegative than O. The H–F bond is more polar than the H–O bond.
- The greater the stability of the conjugate base, the stronger the acid. In the following series, the presence of additional oxygen atoms helps to stabilize the conjugate base by increasing its ability to spread out the negative charge.
- $HOCl < HClO_2 < HClO_3 < HClO_4$   
 weakest acid strongest acid
- The  $\begin{array}{c} \text{:O:} \\ \parallel \\ \text{—C—}\ddot{\text{O}}\text{—H} \end{array}$  group in chemistry is present in acids such as acetic acid (CH<sub>3</sub>COOH). The presence of an extra electronegative oxygen atom helps to pull electron density away from the O–H bond, making the bond more polar. Resonance can also stabilize the conjugate base (CH<sub>3</sub>COO<sup>–</sup>).

- The common ion effect is related to acids and bases. Consider the following information.
  - NaX is a strong electrolyte. It is a soluble ionic compound.
    - $\text{NaX} \rightarrow \text{Na}^+ + \text{X}^-$
  - HX is a weak electrolyte. It is a weak acid.
    - $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$
  - What happens if we have a solution that contains both NaX and HX?
    - The % ionization of HX in this solution is LESS than it would be if HX were in water alone. The presence of additional ions of  $\text{X}^-$  in the solution causes the equilibrium position to shift toward the left (reactants).
  - Calculate the % ionization of  $\text{HC}_2\text{H}_3\text{O}_2$  in 0.10 M  $\text{HC}_2\text{H}_3\text{O}_2$  ( $K_a = 1.8 \times 10^{-5}$ )

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{(0.10-x)} = \frac{(x)(x)}{(0.10)} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-6}$$

$$x = [\text{H}^+] = \sqrt{1.8 \times 10^{-6}} = 0.0013 \text{ M}$$

$$\% \text{ ionization} = \frac{[\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} \times 100\% = \frac{0.0013}{0.10} \times 100\% = 1.3\%$$

- Calculate the % ionization of  $\text{HC}_2\text{H}_3\text{O}_2$  in a solution that contains 0.10 M  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.10 M  $\text{NaC}_2\text{H}_3\text{O}_2$  (which is a buffer).

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{[\text{H}^+](0.10)}{(0.10)} = 1.8 \times 10^{-5}$$

$$[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$$

$$\% \text{ ionization} = \frac{[\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} \times 100\% = \frac{1.8 \times 10^{-5}}{0.10} \times 100\% = 0.018\%$$

- The Components of a Buffer Solution
  - A buffer solution may contain a weak acid (HA) and its conjugate base ( $\text{A}^-$ ).
    - Examples:  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{C}_2\text{H}_3\text{O}_2^-$ , HF and  $\text{F}^-$ ,  $\text{HNO}_2$  and  $\text{NO}_2^-$
  - A buffer solution may contain a weak base (B) and its conjugate acid ( $\text{HB}^+$ ).
    - Examples:  $\text{NH}_3$  and  $\text{NH}_4^+$ ,  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{NH}_2^+$ ,  $\text{C}_5\text{H}_5\text{N}$  and  $\text{C}_5\text{H}_5\text{N}^+$
- Preparing a Buffer Solution that has Equimolar Amounts of Each Component
  - Combine HA with  $\text{A}^-$  (e.g., Mix equal volumes of 1 M HF and 1 M NaF)
  - Combine  $\text{HB}^+$  with B (e.g., Mix equal volumes of 1 M  $\text{NH}_4\text{Cl}$  and 1 M  $\text{NH}_3$ )
  - Combine HA with a strong base so that half of the acid is neutralized (e.g., Mix 100 mL of 1 M  $\text{HC}_2\text{H}_3\text{O}_2$  with 50 mL of 1 M NaOH)
  - Combine B with a strong acid so that half of the base is neutralized (e.g., Mix 100 mL of 1 M  $\text{NH}_3$  with 50 mL of 1 M HCl)

- If you know the concentrations of [HA] and [A<sup>-</sup>] in a buffer solution, there are two ways to calculate the pH
  - Use the  $K_a$  expression and solve for [H<sup>+</sup>]

Example: Calculate the pH of a buffer solution that contains 1.2 M HOCl and 0.80 M NaOCl ( $K_a$  for HOCl =  $3.0 \times 10^{-5}$ )

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{[\text{H}^+](0.80)}{(1.2)} = 3.0 \times 10^{-5}$$

$$[\text{H}^+] = 4.5 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(4.5 \times 10^{-5}) = 4.35$$

- Use the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = -\log(3.0 \times 10^{-5}) + \log\left(\frac{0.80}{1.2}\right) = 4.52 + (-0.18) = 4.34$$

- If you compare the pH of the buffer solution with the  $\text{p}K_a$  of the acid component of the buffer, it will give you information about the  $\frac{[\text{A}^-]}{[\text{HA}]}$  ratio.

- If  $\text{pH} = \text{p}K_a$ , then  $[\text{A}^-] = [\text{HA}]$
- If  $\text{pH} > \text{p}K_a$ , then  $[\text{A}^-] > [\text{HA}]$  (i.e., more base than acid)
- If  $\text{pH} < \text{p}K_a$ , then  $[\text{HA}] > [\text{A}^-]$  (i.e., more acid than base)

- Buffer Capacity – Resistance to Changes in pH

- Suppose you have two buffer solutions with different concentrations of the buffer components. Buffer A contains 1.0 M HNO<sub>2</sub> and 1.0 M NaNO<sub>2</sub>. Buffer B contains 0.10 M HNO<sub>2</sub> and 0.10 M NaNO<sub>2</sub>.

Each of these buffers has the same pH. Which buffer solution (A or B) is more resistant to changes in pH when a strong acid or a strong base is added to it?

The answer is that Buffer A is more resistant to changes in pH because it contains a higher concentration of HNO<sub>2</sub> and NO<sub>2</sub><sup>-</sup>, which are available to react with added H<sup>+</sup> or OH<sup>-</sup> ions.

- The usual pH range of a buffer is  $\text{pH} = \text{p}K_a \pm 1$ . For example, the  $\text{p}K_a$  of acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) is 4.74. A buffer that contains both acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) and acetate (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>) should have a pH range that falls somewhere in between  $\text{pH} = 3.7$  and  $\text{pH} = 5.7$ .
- You may be asked to choose a buffer system that would be most appropriate for achieving a particular pH value. Look at the  $\text{p}K_a$  value of the acid component of the buffer. Choose a buffer system in which the  $\text{p}K_a$  value of the acid is close to the desired pH of the buffer.

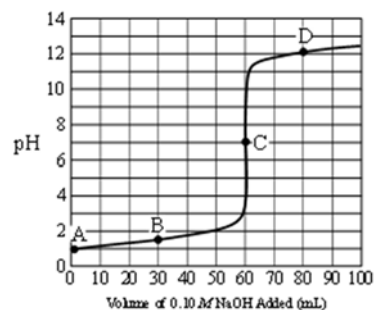


- What happens when a small amount of strong acid or strong base is added to a buffer solution? You should be able to write the net-ionic equation (NIE) that illustrates what happens.
  - Suppose the buffer contains a mixture of HX and  $X^-$ 
    - If a strong acid is added, the NIE is  $H^+ + X^- \rightarrow HX$  or  $H_3O^+ + X^- \rightarrow HX + H_2O$
    - If a strong base is added, the NIE is  $OH^- + HX \rightarrow X^- + H_2O$
  - Suppose the buffer contains a mixture of  $HB^+$  and B
    - If a strong acid is added, the NIE is  $H^+ + B \rightarrow HB^+$  or  $H_3O^+ + B \rightarrow HB^+ + H_2O$
    - If a strong base is added, the NIE is  $OH^- + HB^+ \rightarrow B + H_2O$
- In an acid-base titration experiment that involves a 1-to-1 mole ratio between the acid and the base (e.g.,  $HA + NaOH \rightarrow H_2O + NaA$ ), you can use the equation  $(M_a)(V_a) = (M_b)(V_b)$  to perform calculations such as the following.
  - Calculate the volume of titrant that is required to reach the equivalence point.
  - Calculate the concentration of the acid (or the base) that was used in the titration.

- Acid-Base Titrations

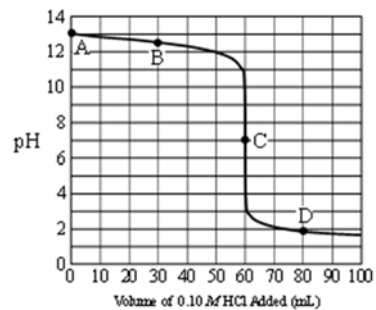
- Strong Acid – Strong Base

- General shape of titration curve is shown at right.
- $pH = 7$  at the equivalence point because the salt that is produced in the reaction is neutral. (e.g., NaCl)
- There is nothing special about the half-equivalence pt.
- If the mole ratio between the acid and the base is 1-to-1, you can use  $(M_a)(V_a) = (M_b)(V_b)$
- $V_b$  = volume of base required to reach the eq. pt.



- Strong Base – Strong Acid

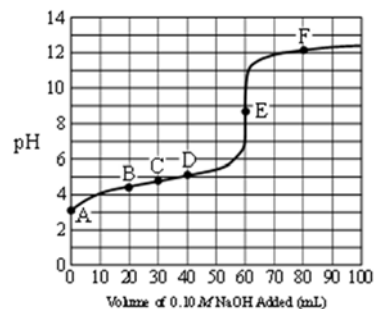
- General shape of titration curve is shown at right.
- $pH = 7$  at the equivalence point because the salt that is produced in the reaction is neutral. (e.g., NaCl)
- There is nothing special about the half-equivalence pt.
- If the mole ratio between the acid and the base is 1-to-1, you can use  $(M_a)(V_a) = (M_b)(V_b)$
- $V_a$  = volume of acid required to reach the eq. pt.



- Acid-Base Titrations (continued)

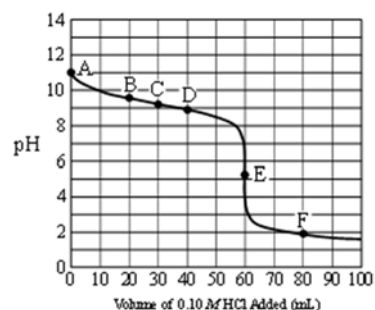
- Weak Acid – Strong Base

- General shape of titration curve is shown at right.
    - $\text{pH} > 7$  at the equivalence point because the salt that is produced in the reaction is basic. (e.g., NaF,  $\text{NaC}_2\text{H}_3\text{O}_2$ , or NaOCl)
    - If  $\text{pH} < \text{p}K_a$ ,  $[\text{HA}] > [\text{A}^-]$  (e.g., Point B on the graph)
    - If  $\text{pH} = \text{p}K_a$ ,  $[\text{HA}] = [\text{A}^-]$  at the half-equivalence point. (Point C on the graph)
    - If  $\text{pH} > \text{p}K_a$ ,  $[\text{A}^-] > [\text{HA}]$  (e.g., Point D on the graph)
    - If the mole ratio between the acid and the base is 1-to-1, you can use  $(M_a)(V_a) = (M_b)(V_b)$
    - $V_b$  = volume of base required to reach the eq. pt.



- Weak Base – Strong Acid

- General shape of titration curve is shown at right.
    - $\text{pH} < 7$  at the equivalence point because the salt that is produced in the reaction is acidic. (e.g.,  $\text{NH}_4\text{Cl}$ ,  $\text{CH}_3\text{NH}_3\text{Cl}$ , or  $(\text{CH}_3)_3\text{NHCl}$ )
    - If  $\text{pH} > \text{p}K_a$ ,  $[\text{B}] > [\text{HB}^+]$  (e.g., Point B on the graph)
    - If  $\text{pH} = \text{p}K_a$ ,  $[\text{HB}^+] = [\text{B}]$  at the half-equivalence point. (Point C on the graph)
    - If  $\text{pH} < \text{p}K_a$ ,  $[\text{HB}^+] > [\text{B}]$  (e.g., Point D on the graph)
    - If the mole ratio between the acid and the base is 1-to-1, you can use  $(M_a)(V_a) = (M_b)(V_b)$
    - $V_a$  = volume of acid required to reach the eq. pt.



- The equivalence point in the titration occurs when moles of acid = moles of base

Calculations related to the equivalence point are based on moles (i.e., volume  $\times$  molarity)

It does not matter if the substance that you are titrating is strong or weak. It's all about the moles.

- 100 mL of 1 M HCl (strong acid) requires 100 mL of 1 M NaOH to reach the eq. pt.
  - 100 mL of 1 M  $\text{HC}_2\text{H}_3\text{O}_2$  (weak acid) requires 100 mL of 1 M NaOH to reach the eq. pt.
  - 100 mL of 1 M NaOH (strong base) requires 100 mL of 1 M HCl to reach the eq. pt.
  - 100 mL of 1 M  $\text{NH}_3$  (weak base) requires 100 mL of 1 M HCl to reach the eq. pt.

- You may be asked to choose an indicator that would be most appropriate for signaling the end point in a titration experiment. The pH rises sharply at the equivalence point. A good indicator should change color near (or at) the equivalence point. Look at the  $\text{p}K_a$  value of the indicator or the pH range in which the color change occurs. Choose an indicator that experiences a color change very close to the pH of the solution at the equivalence point.

- Saturated Solutions and the  $K_{sp}$  Expression

- In a saturated solution, the rate of dissolution is equal to the rate of crystallization
- Write the net-ionic equation for the dissolution of each compound.
  - $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$
  - $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2 \text{OH}^{-}(aq)$
  - $\text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2 \text{Ag}^{+}(aq) + \text{CO}_3^{2-}(aq)$
- Write the  $K_{sp}$  expression for each of the compounds above.
  - $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
  - $K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$
  - $K_{sp} = [\text{Ag}^{+}]^2[\text{CO}_3^{2-}]$

- Solubility and  $K_{sp}$

- If you are given the solubility of a compound (in either g/L or mol/L), you can calculate the  $K_{sp}$  value. You may need to convert the solubility from units of g/L into units of mol/L.
- Pay attention to the stoichiometry (mole ratio) for the compound and the dissolved ions. If the molar solubility of the compound =  $s$ , then
  - $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (s)(s) = s^2$
  - $K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2 = (s)(2s)^2 = 4s^3$
  - $K_{sp} = [\text{Ag}^{+}]^2[\text{CO}_3^{2-}] = (2s)^2(s) = 4s^3$
- If you compare different compounds that have the same cation-to-anion mole ratio, the one with the greatest value for  $K_{sp}$  will have the greatest molar solubility in water.

$\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ )  
most soluble

$\text{AgBr}$  ( $K_{sp} = 5.0 \times 10^{-13}$ )

$\text{AgI}$  ( $K_{sp} = 8.3 \times 10^{-17}$ )  
least soluble

- Calculating solubility from  $K_{sp}$

Example: Calculate the molar solubility of  $\text{Mg}(\text{OH})_2$  ( $K_{sp} = 1.8 \times 10^{-11}$ ).

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2 = (s)(2s)^2 = 4s^3 = 1.8 \times 10^{-11}$$

$$s = \sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = 1.7 \times 10^{-4} \text{ M}$$

- Calculating  $K_{sp}$  from solubility

Example: The solubility of  $\text{Ag}_2\text{SO}_4$  is 0.016 M. Calculate the value of  $K_{sp}$  for  $\text{Ag}_2\text{SO}_4$ .

$$K_{sp} = [\text{Ag}^{+}]^2[\text{SO}_4^{2-}] = (2s)^2(s) = (0.032)^2(0.016) = 1.6 \times 10^{-5}$$

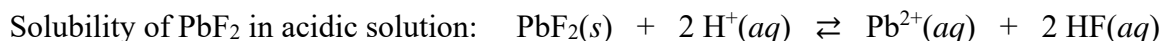
- Factors that affect solubility

- The common ion effect

- The solubility of a slightly soluble salt is decreased by the presence of a second solute that contains a common ion. For example, the solubility of  $\text{AgCl}(s)$  is lower in a solution that already contains either  $\text{Ag}^+(aq)$  or  $\text{Cl}^-(aq)$ .

- The effect of pH

- If a slightly soluble salt contains a basic anion (such as  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CN}^-$ , or  $\text{PO}_4^{3-}$ ), the solubility of that salt will be greater in an acidic solution.
    - Example:  $\text{PbF}_2(s)$  is more soluble in an acidic solution than it is in pure water. Use net-ionic equations to explain why this occurs.



In acidic solution,  $[\text{F}^-]$  decreases because it reacts with  $\text{H}^+$  ions to form HF. The solubility equilibrium for  $\text{PbF}_2$  shifts toward the products. Therefore  $\text{PbF}_2$  is more soluble in an acidic solution than it is in pure water.

- Will a Precipitate Form or Not? (Comparing  $Q$  vs.  $K_{sp}$ )

You may be asked to predict whether or not a precipitate will form when two solutions are mixed together. Follow these instructions.

- If two solutions are mixed together, calculate the molarity of each ion in the final solution. This can be done by using the equation  $(M_c)(V_c) = (M_d)(V_d)$  where  $c$  = concentrated and  $d$  = dilute
  - Calculate the value of  $Q$ , by plugging in the values for the molarity of each ion into the  $K_{sp}$  expression for the salt.
  - If the value of  $Q < K_{sp}$ , then a precipitate will not form.
  - If the value of  $Q > K_{sp}$ , then a precipitate will form.

Example: Will a precipitate form when 100. mL of  $1.8 \times 10^{-6} M \text{Pb}(\text{NO}_3)_2(aq)$  is mixed with 100. mL of  $2.4 \times 10^{-6} M \text{Na}_2\text{CO}_3(aq)$ ? The  $K_{sp}$  for  $\text{PbCO}_3$  is equal to  $7.4 \times 10^{-14}$ .

$$[\text{Pb}^{2+}] \text{ in the final solution: } \frac{(0.100 \text{ L})(1.8 \times 10^{-6} \text{ mol/L})}{(0.200 \text{ L})} = 9.0 \times 10^{-7} \text{ mol/L}$$

$$[\text{CO}_3^{2-}] \text{ in the final solution: } \frac{(0.100 \text{ L})(2.4 \times 10^{-6} \text{ mol/L})}{(0.200 \text{ L})} = 1.2 \times 10^{-6} \text{ mol/L}$$

$$Q = [\text{Pb}^{2+}][\text{CO}_3^{2-}] = (9.0 \times 10^{-7})(1.2 \times 10^{-6}) = 1.1 \times 10^{-12}, \text{ which is greater than } 7.4 \times 10^{-14}.$$

Since  $Q > K_{sp}$ , a precipitate of  $\text{PbCO}_3(s)$  will form when these solutions are mixed.