



Unit Overview

Topic 8.1: Introduction to Acids and Bases

Learning Objective: Calculate the values of pH and pOH, based on K_w and the concentration of all species present in a neutral solution of water.

Essential Knowledge:

- The concentrations of hydronium ion and hydroxide ion are often reported as pH and pOH, respectively.
EQN: $\text{pH} = -\log[\text{H}_3\text{O}^+]$
EQN: $\text{pOH} = -\log[\text{OH}^-]$
The terms “hydrogen ion” and “hydronium ion” and the symbols $\text{H}^+(\text{aq})$ and $\text{H}_3\text{O}^+(\text{aq})$ are often used interchangeably for the aqueous ion of hydrogen. Hydronium ion and $\text{H}_3\text{O}^+(\text{aq})$ are preferred, but $\text{H}^+(\text{aq})$ is also accepted on the AP Exam
- Water autoionizes with an equilibrium constant K_w .
EQN: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 25°C
- In pure water, $\text{pH} = \text{pOH}$ is called a neutral solution. At 25°C , $\text{p}K_w = 14.0$ and thus $\text{pH} = \text{pOH} = 7.0$.
EQN: $\text{p}K_w = 14 = \text{pH} + \text{pOH}$ at 25°C
- The value of K_w is temperature dependent, so the pH of pure, neutral water will deviate from 7.0 at temperatures other than 25°C .

Topic 8.2: pH and pOH of Strong Acids and Bases

Learning Objective: Calculate pH and pOH based on concentrations of all species in a solution of a strong acid or a strong base.

Essential Knowledge:

- Molecules of a strong acid (e.g., HCl, HBr, HI, HClO_4 , H_2SO_4 , and HNO_3) will completely ionize in aqueous solution to produce hydronium ions. As such, the concentration of H_3O^+ in a strong acid solution is equal to the initial concentration of the strong acid, and thus the pH of the strong acid solution is easily calculated.
- When dissolved in solution, strong bases (e.g., group I and II hydroxides) completely dissociate to produce hydroxide ions. As such, the concentration of OH^- in a strong base solution is equal to the initial concentration of the strong base, and thus the pOH (and pH) of the strong base solution is easily calculated.

Topic 8.3: Weak Acid and Base Equilibria

Learning Objective: Explain the relationship among pH, pOH, and concentrations of all species in a solution of a monoprotic weak acid or weak base.

Essential Knowledge:

- Weak acids react with water to produce hydronium ions. However, molecules of a weak acid will only partially ionize in this way. In other words, only a small percentage of the molecules of a weak acid are ionized in a solution. Thus, the concentration of H_3O^+ is much less than the initial concentration of the molecular acid, and the vast majority of the acid molecules remain un-ionized.
- A solution of a weak acid involves equilibrium between an un-ionized acid and its conjugate base. The equilibrium constant for this reaction is K_a , often reported as $\text{p}K_a$. The pH of a weak acid solution can be determined from the initial acid concentration and the $\text{p}K_a$

$$\text{EQN: } K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{EQN: } \text{p}K_a = -\log K_a$$

- Weak bases react with water to produce hydroxide ions in solution. However, ordinarily just a small percentage of the molecules of a weak base in solution will ionize in this way. Thus, the concentration of OH^- in the solution does not equal the initial concentration of the base, and the vast majority of the base molecules remain un-ionized.
- A solution of a weak base involves equilibrium between an un-ionized base and its conjugate acid. The equilibrium constant for this reaction is K_b , often reported as $\text{p}K_b$. The pH of a weak base solution can be determined from the initial base concentration and the $\text{p}K_b$.

$$\text{EQN: } K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]}$$

$$\text{EQN: } \text{p}K_b = -\log K_b$$

- The percent ionization of a weak acid (or base) can be calculated from its pK_a (pK_b) and the initial concentration of the acid (base).

Topic 8.4: Acid-Base Reactions and Buffers

Learning Objective: Explain the relationship among the concentrations of major species in a mixture of weak and strong acids and bases.

Essential Knowledge:

- When a strong acid and a strong base are mixed, they react quantitatively in a reaction represented by the equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$. The pH of the resulting solution may be determined from the concentration of excess reagent.
- When a weak acid and a strong base are mixed, they react quantitatively in a reaction represented by the equation: $HA(aq) + OH^-(aq) \rightleftharpoons A^-(aq) + H_2O(l)$.
If the weak acid is in excess, then a buffer solution is formed, and the pH can be determined from the Henderson-Hasselbalch (H-H) equation. If the strong base is in excess, then the pH can be determined from the moles of excess hydroxide ion and the total volume of solution. If they are equimolar, then the (slightly basic) pH can be determined from the equilibrium represented by the equation:
 $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$.
- When a weak base and a strong acid are mixed, they will react quantitatively in a reaction represented by the equation:
 $B(aq) + H_3O^+(aq) \rightleftharpoons HB^+(aq) + H_2O(l)$.
If the weak base is in excess, then a buffer solution is formed, and the pH can be determined from the H-H equation. If the strong acid is in excess, then the pH can be determined from the moles of excess hydronium ion and the total volume of solution. If they are equimolar, then the (slightly acidic) pH can be determined from the equilibrium represented by the equation:
 $HB^+(aq) + H_2O(l) \rightleftharpoons B(aq) + H_3O^+(aq)$.
- When a weak acid and a weak base are mixed, they will react to an equilibrium state whose reaction may be represented by the equation:
 $HA(aq) + B(aq) \rightleftharpoons A^-(aq) + HB^+(aq)$.

Topic 8.5: Acid-Base Titrations

Learning Objective: Explain results from the titration of a mono- or polyprotic acid or base solution, in relation to the properties of the solution and its components.

Essential Knowledge:

- An acid-base reaction can be carried out under controlled conditions in a titration. A titration curve, plotting pH against the volume of titrant added, is useful for summarizing results from a titration.
- At the equivalence point, the number of moles of titrant added is equal to the number of moles of analyte originally present. This relationship can be used to obtain the concentration of the analyte. This is the case for titrations of strong acids/bases and weak acids/bases.
- For titrations of weak acids/bases, it is useful to consider the point halfway to the equivalence point, that is, the half-equivalence point. At this point, there are equal concentrations of each species in the conjugate acid-base pair, for example, for a weak acid $[HA] = [A^-]$. Because $pH = pK_a$ when the conjugate acid and base have equal concentrations, the pK_a can be determined from the pH at the half-equivalence point in a titration.
- For polyprotic acids, titration curves can be used to determine the number of acidic protons. In doing so, the major species present at any point along the curve can be identified, along with the pK_a associated with each proton in a weak polyprotic acid.

Topic 8.6: Molecular Structure of Acids and Bases

Learning Objective: Explain the relationship between the strength of an acid or base and the structure of the molecule or ion.

Essential Knowledge:

- The protons on a molecule that will participate in acid-base reactions, and the relative strength of these protons, can be inferred from the molecular structure.
 - o Strong acids (such as HCl, HBr, HI, $HClO_4$, H_2SO_4 , and HNO_3) have very weak conjugate bases that are stabilized by electronegativity, inductive effects, resonance, or some combination thereof.
 - o Carboxylic acids are one common class of weak acid.
 - o Strong bases (such as group I and II hydroxides) have very weak conjugate acids.
 - o Common weak bases include nitrogenous bases such as ammonia as well as carboxylate ions.

- o Electronegative elements tend to stabilize the conjugate base relative to the conjugate acid, and so increase acid strength.

Topic 8.7: pH and pK_a

Learning Objective: Explain the relationship between the predominant form of a weak acid or base in solution at a given pH and the pK_a of the conjugate acid or the pK_b of the conjugate base.

Essential Knowledge:

- The protonation state of an acid or base (i.e., the relative concentrations of HA and A^-) can be predicted by comparing the pH of a solution to the pK_a of the acid in that solution. When solution pH < acid pK_a , the acid form has a higher concentration than the base form. When solution pH > acid pK_a , the base form has a higher concentration than the acid form.
- Acid-base indicators are substances that exhibit different properties (such as color) in their protonated versus deprotonated state, making that property respond to the pH of a solution.

Topic 8.8: Properties of Buffers

Learning Objective: Explain the relationship between the ability of a buffer to stabilize pH and the reactions that occur when an acid or a base is added to a buffered solution.

Essential Knowledge:

- A buffer solution contains a large concentration of both members in a conjugate acid-base pair. The conjugate acid reacts with added base and the conjugate base reacts with added acid. These reactions are responsible for the ability of a buffer to stabilize pH.

Topic 8.9: Henderson-Hasselbalch Equation

Learning Objective: Identify the pH of a buffer solution based on the identity and concentrations of the conjugate acid-base pair used to create the buffer.

Essential Knowledge:

- The pH of the buffer is related to the pK_a of the acid and the concentration ratio of the conjugate acid-base pair. This relation is a consequence of the equilibrium expression associated with the dissociation of a weak acid, and is described by the Henderson-Hasselbalch equation. Adding small amounts of acid or base to a buffered solution does not significantly change the ratio of $[A^-]/[HA]$ and thus does not significantly change the solution pH. The change in pH on addition of acid or base to a buffered solution is therefore much less than it would have been in the absence of the buffer.
- EQN: $pH = pK_a + \log \log \frac{[A^-]}{[HA]}$

Topic 8.10: Buffer Capacity

Learning Objective: Explain the relationship between the buffer capacity of a solution and the relative concentrations of the conjugate acid and conjugate base components of the solution.

Essential Knowledge:

- Increasing the concentration of the buffer components (while keeping the ratio of these concentrations constant) keeps the pH of the buffer the same but increases the capacity of the buffer to neutralize added acid or base.
- When a buffer has more conjugate acid than base, it has a greater buffer capacity for addition of added base than acid. When a buffer has more conjugate base than acid, it has a greater buffer capacity for addition of added acid than base.

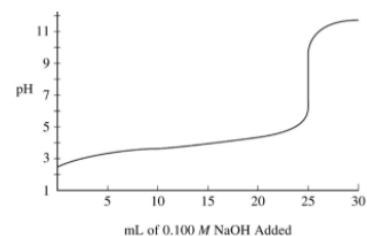
Important understandings for this test:

1. Understand the meaning of K_w and that its value at 25° is 1.00×10^{-14} but changes at different temperatures. But no matter the temperature, $[H_3O^+] = [OH^-]$ and $pH + pOH = pK_w$
2. What are the strong acids. Remember, strong acids ionize 100% meaning that their $[H_3O^+] = [acid]$.
3. $pH = -\log [H_3O^+]$. So, if $pH = 1$, $[H_3O^+] = 1 \times 10^{-1}$ M. If $pH = 5$, $[H_3O^+] = 1 \times 10^{-5}$ M. An approximation of the pH is the positive value of the exponent of the $[H_3O^+]$. Remember, more acid means LOWER pH. Less acidic means HIGHER pH.
4. What are the strong bases? Remember, strong bases ionize completely, even strong bases with more than one OH^- ion. So with that in mind, what would be the $[OH^-]$ in a 1.5 M NaOH solution? A 1.5 M $Sr(OH)_2$ solution?

5. Soluble salts can contain the conjugate acid of a base or the conjugate base of an acid. For example, NaNO_2 contains the conjugate base (NO_2^-) of nitrous acid (HNO_2). KClO_2 contains the conjugate base of chlorous acid (HClO_2). NH_4Cl contains the conjugate acid (NH_4^+) of ammonia (NH_3). In solution, the Na^+ , K^+ , and Cl^- are spectator ions and do not interfere with the acid-base equilibrium. Ions from strong acids or strong bases are neutral (e.g., Na^+ , K^+ , and Cl^- are ions in NaOH , KOH , and HCl , all of which are strong acids or bases. So Na^+ , K^+ , and Cl^- are all neutral.)
6. The smaller the K_a value, the weaker the acid. The smaller the K_b value, the weaker the base. The weaker an acid, the stronger its conjugate base. Remember, $K_a \times K_b = K_w$. So K_a and K_b are inversely related. So for example, look up the K_a values for acetic, formic, and lactic acids. Which is the strongest acid? Which will have the strongest conjugate base?
7. When a weak acid is titrated with a strong base, the OH^- from the base reacts with the acid. When a weak base is titrated with a strong acid, the H^+ from the acid reacts with the base. When a strong acid and a strong base react, they form a salt (ionic compound) and water.
8. At the half equivalence point (the point where a solution is titrated and volume of titrant added is half the volume of titrant needed to reach the equivalence point), the $[\text{acid}] = [\text{conjugate base}]$ if an acid is being titrated and the $[\text{base}] = [\text{conjugate acid}]$ if a base is being titrated. So according to the Henderson-Hasselbach equation, the $\text{pH} = \text{p}K_a$ at the half equivalence point (see below).

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conj base}]}{[\text{acid}]}$$

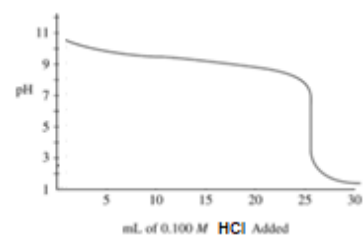
9. In the titration curve to the right, what volume of 0.100 M NaOH has been added and what is the pH at the half equivalence point? Is the analyte a strong or weak acid or base? Is the titrant a strong or weak acid or base? What is the approximate $\text{p}K_a$ of the analyte? Using the indicator chart below, what would be the best indicator for this titration?



acid-base indicator table

indicator	pH range	color for weak acid	color for conjugate base
methyl orange	4-6	orange	yellow
bromophenol blue	6-7	yellow	blue
thymol blue	8-9	yellow	blue
phenolphthalein	9-10	colorless	pink
alizarin yellow	10-12	yellow	red

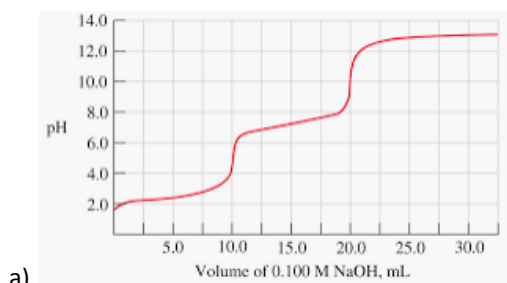
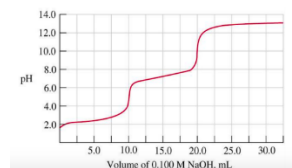
10. In the titration curve to the right, what volume of 0.100 M HCl has been added and what is the pH at the half equivalence point? Is the analyte a strong or weak acid or base? Is the titrant a strong or weak acid or base? What is the approximate $\text{p}K_b$ of the analyte? Using the indicator chart above, what would be the best indicator for this titration?



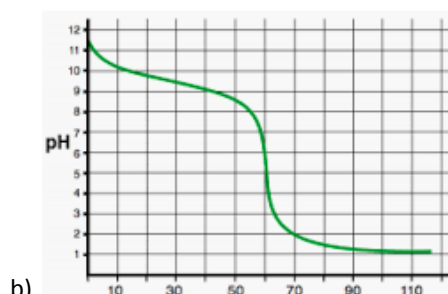
11. Buffers are solutions that contain both a weak acid and its conjugate base or a weak base and its conjugate acid. Buffers help maintain the pH of a solution because the acid can neutralize limited amounts of added base and the base can neutralize limited amounts of added acid. The amount of acid or base a buffer can neutralize is called the “buffering capacity” of the buffer. A buffer has optimal buffering action (ability to neutralize both added acids and bases) when the concentrations of the conjugate acid-base pair are equal.
12. Be able to write net ionic equations. (Remember, water is a liquid, so it gets included in net ionic equations!)
 ex) write the net ionic equation for the following reactions:
 a) sulfuric acid reacting with sodium hypochlorite (sulfuric acid after only losing 1st proton)
 b) magnesium acetate reacting with lithium hydroxide
13. Be able to calculate the number of moles and grams of solute in a solution given its volume and molarity.
14. What is an electrolyte? What is the difference between a strong electrolyte and a weak electrolyte?
15. Don't forget the basics of equilibrium: $K \gg 1$ means product-favored; $K \ll 1$ means reactant-favored. Weak acid and base hydrolysis equilibria are always reactant favored.
16. Be able to easily convert among $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH.

More Practice

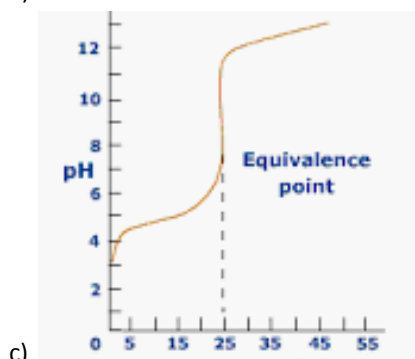
- What are the pH, pOH, $[H_3O^+]$, and $[OH^-]$ for a 4.12×10^{-2} M solution of HNO_3 ?
- a) What are the $[H_3O^+]$ and $[OH^-]$ in pure water at $25^\circ C$ when the K_w is 1.00×10^{-14} ? b) What are the pH and pOH of water at $25^\circ C$? c) What are the $[H_3O^+]$ and $[OH^-]$ in pure water at $10^\circ C$ when the K_w is 2.93×10^{-15} ? d) What are the pH and pOH of water at $0^\circ C$ when the $K_w = 1.14 \times 10^{-15}$?
- At $50^\circ C$, $K_w = 5.476 \times 10^{-14}$. What are $[H_3O^+]$ and $[OH^-]$ as well as the pH and pOH of this solution? Does $pH + pOH = 14$ at this temperature?
- Identify the weak acids in the following list: HCl , HF , $HClO$, $HClO_4$, HNO_2 , $HC_2H_3O_2$, and H_2SO_4 .
- What is meant by weak when referring to acids or bases?
- Write the reaction of NH_4^+ with water. Write the reaction of NH_3 with water. Write the K_a equation for NH_4^+ . Write the K_b equation for NH_3 . What is the relationship between K_a and K_b for these two substances?
- Perform the following calculations for a 0.25 M solution of NH_3 ($K_b = 1.8 \times 10^{-5}$): a) What is the K_a of the conjugate acid?, b) What is the pH of the solution?, c) What is the percent ionization of the NH_3 ?
- Write the complete neutralization reaction as well as the net ionic equation for a strong acid reacting with a strong base. Choose any strong acid and strong base you like.
- What mass of solid $NaOH$ must be added to 15.3 mL of 1.5 M HCl to completely neutralize the acid? Assume the volume change by adding the solid base is minimal.
- What is the pH of 150. mL of a 0.50 M $HC_2H_3O_2$ solution after the following number of moles of solid $NaOH$ are added to the solution: a) 0 moles $NaOH$, b) 0.015 moles $NaOH$, c) 0.075 moles $NaOH$, d) 0.10 moles $NaOH$? Assume the $NaOH$ does not change the volume of solution appreciably.
- Which number of moles of added $NaOH$ is acting in the buffer region of the weak acid titration?
- Use $>$, >7 , or <7 as your answers for the following titration questions. What is the pH at the equivalence point for the following titrations (all are monoprotic acids and monoprotic bases): a) A strong acid titrated with a strong base; b) A weak acid titrated with a strong base; c) A weak base titrated with a strong acid?
- A student titrates 30. mL of a weak acid with a strong base to the equivalence point. The student then adds the titrated solution to a beaker containing 30. mL of untitrated weak acid and measures the pH of the resulting solution to be 7.46. Using your master chemistry knowledge and the table on page A22 of the appendix in your book, what is the identity of the acid?
- Does the titration curve to the right show the titration of a monoprotic, diprotic, or triprotic acid? How do you know?
- Which of the following titration curves show: a) a monoprotic weak base being titrated with a strong acid? b) a monoprotic weak acid being titrated with a strong base? c) a polyprotic acid being titrated with a strong base? d) a monoprotic strong base being titrated with a weak acid?



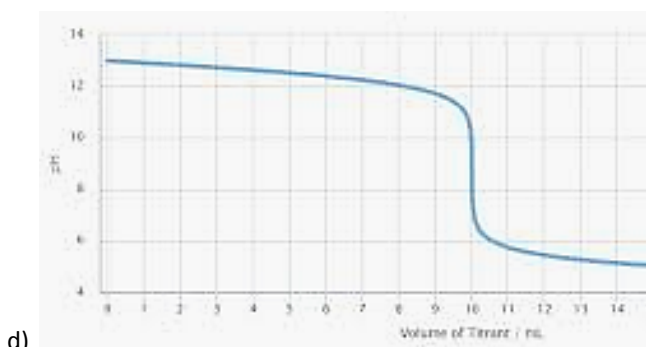
a)



b)



c)



d)

16. Rate the following in order of acid strength: HNO_2 , Br^- , H_2O , HClO_4 , HOCl
17. Which of the following ions cannot act as a base? NO_2^- , CN^- , F^- , ClO_4^- , $\text{C}_2\text{H}_3\text{O}_2^-$, HCO_3^-
18. Which of the following ion can act as both an acid and a base (we call this "amphoteric")? NO_2^- , CN^- , F^- , ClO_4^- , $\text{C}_2\text{H}_3\text{O}_2^-$, HCO_3^-
19. Which of the following would have the greater buffer capacity: a solution containing 0.50 M HCN and 0.50 M KCN or a solution containing 0.75 M HCN and 1.00 M KCN?
20. Calculate the pH of both solutions in problem 19. (You will need to look up the K_a of HCN to solve this problem.)
21. If 12.0 mL of 0.50 M KOH is added to 125 mL of a buffer system containing 0.75 M HCN and 1.00 M KCN, what is the pH of the resulting solution? How does this pH compare to the pH of the original buffer solution (from problem 20)?

Answers to the "More Practice" Problems

- 1) $\text{pH} = 1.385$, $\text{pOH} = 12.615$, $[\text{H}_3\text{O}^+] = 4.12 \times 10^{-2} \text{M}$, $[\text{OH}^-] = 2.43 \times 10^{-13} \text{M}$
- 2) a) $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{M}$ (this changes at different temperatures, but $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ always for water!); b) $\text{pH} = \text{pOH} = 7$ (this changes at different temperatures, but $\text{pH} = \text{pOH}$ always for water!); c) $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 5.41 \times 10^{-8} \text{M}$; d) $\text{pH} = \text{pOH} = 7.472$ (shout out to Andres for the correction)
- 3) $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 2.34 \times 10^{-7} \text{M}$; $\text{pH} = \text{pOH} = 6.6308$; no! $\text{pH} + \text{pOH} = 13.2616$
- 4) HF, HClO, HNO_2 , $\text{HC}_2\text{H}_3\text{O}_2$
- 5) Incomplete ionization
- 6) $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ $K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$
- $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ $K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]}$
- $K_a \times K_b = K_w = 1.00 \times 10^{-14}$ (@ 25°C)
- 7 a) 5.6×10^{-10} b) 11.33 c) 0.85%
- 8) $\text{HCl} + \text{NaOH} \rightleftharpoons \text{HOH} + \text{NaCl}$
 $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{HOH}$
- 9) 0.918 g NaOH
- 10 a) 2.52 b) 4.14 c) 9.22 d) 13.22
- 11) 0.015 mol NaOH
- 12 a) 7 b) >7 c) <7
- 13) HOCl
- 14) diprotic because two equivalence points; 1) $\text{H}_2\text{A} + \text{OH}^- \rightleftharpoons \text{HA}^- + \text{HOH}$; 2) $\text{HA}^- + \text{OH}^- \rightleftharpoons \text{A}^- + \text{HOH}$
- 15 a) B b) C c) A d) D
- 16) $\text{Br}^- < \text{H}_2\text{O} < \text{HOCl} < \text{HNO}_2 < \text{HClO}_4$
- 17) ClO_4^-
- 18) HCO_3^-
- 19) The solution with 0.75 M HCN and 1.00 M KCN (no work, just higher concentrations)
- 20) 0.50 M HCN and 0.50 M KCN: 9.21 and 0.75 M HCN and 1.00 M KCN: 9.33
- 21) 9.38; higher (but not by much) than untitrated solution.