CHAPTER 16 – Acid-Base Equilibria

Section 16.1 – Acids and Bases: A Brief Review

(a) Define an acid and a base, according to the Arrhenius definition.

acid = ____

base = ____

(b) Write the products of each chemical reaction below, which involves the dissociation of each reactant into aqueous ions.

$$HCl(g) \xrightarrow{H_2O}$$

$$NaOH(s) \xrightarrow{H_2O}$$

Section 16.2 – Brønsted-Lowry Acids and Bases

(a) The Arrhenius definition is limited to aqueous solutions. A more general definition of acids and bases is the Brønsted-Lowry definition, which involves the transfer of __________ ions from one substance to another.

(b) Draw the Lewis dot structures for both water and the hydronium ion.

(c) Chemists use the symbols H^+ and H_3O^+ interchangeably when referring to the ion that determines the acidity of a solution. You will also hear the H^+ ion referred to by name as a _______________________.

(d) Write the formulas for the two products formed in this chemical reaction.

$$HCl(g) \quad + \quad H_2O(l) \longrightarrow$$

(e) In part (d), HCl behaves as ______________ because it _________________ H^+,

and water behaves as __________________ because it _________________ H^+.

(f) Does the Brønsted-Lowry definition of acids and bases require that the reaction take place in aqueous solution? ___________

(g) Acid-base chemistry can occur in the gas phase. Write the formulas for two gases that react together to form solid ammonium chloride. This is visible as smoke when solutions of these two substances are brought close together in the laboratory. Identify the acid and the base.

The acid is ___________ because it is a H^+ _______________

The base is __________ because it is a H^+ _______________

(h) Write the formulas for the two products formed in this chemical reaction.

$$NH_3(aq) + H_2O(l) \rightleftharpoons$$

(i) In part (h), NH_3 behaves as ______________ because it _________________ H^+,

and water behaves as __________________ because it _________________ H^+.

(j) A Brønsted-Lowry acid must have a ______________ atom that it can lose as a positive ion.

(k) A Brønsted-Lowry base must have a ____________________ that it can use to bind the H^+ ion.

(l) Water is an example of an amphiprotic substance. What does it mean to be amphiprotic?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$$

(m) Looking at the reactants from the equation shown above,

__________ = acid __________ = base

Looking at the products from the equation shown above,

__________ = conjugate acid __________ = conjugate base

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

(n) Looking at the reactants from the equation shown above,

__________ = acid __________ = base

Looking at the products from the equation shown above,

__________ = conjugate acid __________ = conjugate base

(o) Every acid has a conjugate base, formed by _________________ a proton from the acid.

Every base has a conjugate acid, formed by _________________ a proton to the base.

(p) Write the chemical formula for the conjugate base of each acid and the conjugate acid of each base.

Acid	**Conjugate Base**
HF	
H_2S	
PH_4^+	
HCO_3^-	
HPO_4^{2-}	
H_2O	

Base	**Conjugate Acid**
CH_3NH_2	
CN^-	
SO_4^{2-}	
HCO_3^-	
HPO_4^{2-}	
H_2O	

(q) The hydrogen carbonate ion (aka bicarbonate) is an amphiprotic ion.

Write an equation for bicarbonate behaving as an acid when it reacts with water.

Write an equation for bicarbonate behaving as a base when it reacts with water.

(r) The ____________________ an acid is, the __________________ its conjugate base is.

The ____________________ a base is, the __________________ its conjugate acid is.

(s) Describe the difference between a strong acid and a weak acid, in terms of how they behave in water (i.e., the extent to which they dissociate into ions in water).

(t) You should memorize the seven strong acids. They can be found in Table 4.2 on page 125. Write their formulas in the spaces provided.

hydrochloric acid = ________ chloric acid = ____________ sulfuric acid = ____________

hydrobromic acid = ________ perchloric acid = __________

hydroiodic acid = _________ nitric acid = ______________

(u) A few examples of weak acids are listed below. Some of these can be found in Table 16.2 on page 667. Write their formulas in the spaces provided.

chlorous acid = ___________

hydrofluoric acid = ________

nitrous acid = ____________

hydrocyanic acid = ________

hypochlorous acid = __________

benzoic acid = ______________

acetic acid (ethanoic acid) = ______________

carbonic acid = ______________

(v) Why does the nitrate ion have negligible basicity?

(w) Why is the fluoride ion classified as a stronger base than the chloride ion?

(x) For each of the following reactions, write a lowercase "a" under the weaker acid and a capital "A" under the stronger acid. Then write a lowercase "b" under the weaker base and a capital "B" under the stronger base. Use Figure 16.3 on page 657 to help you. Predict whether the equilibrium lies to the left (K < 1) or to the right (K > 1).

Acid-Base Reaction	Does the equilibrium lie to the left or to the right?
$HSO_4^- + CO_3^{2-} \rightleftharpoons HCO_3^- + SO_4^{2-}$	
$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$	
$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$	
$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$	
$HC_2H_3O_2 + PO_4^{3-} \rightleftharpoons HPO_4^{2-} + C_2H_3O_2^-$	

Section 16.3 – The Autoionization of Water

(a) We have already seen that H_2O is amphiprotic, capable of acting as an acid or as a base. Write an equation to show how one water molecule can donate a proton to another water molecule.

The equilibrium for the reaction you just wrote is strongly favored toward the left. We know this because the value of the equilibrium constant (K_w) is very small. This equilibrium constant is called the ion-product constant for water. At 25°C it has a value of 1.0×10^{-14}

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \quad \text{(at 25°C)}$$

The auto-ionization of water can also be written as follows.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

This is a very important relationship that allows you to calculate $[H^+]$, $[OH^-]$, pH, and pOH.

(b) In a neutral solution (at 25°C), $[H^+]$ = _____________ M and $[OH^-]$ = _____________ M

In an acidic solution, $[H^+]$ is _________________ than $[OH^-]$.

In a basic solution, $[H^+]$ is __________________ than $[OH^-]$.

(c) Fill in the table below with the missing information.

$[H^+]$	$[OH^-]$	Acidic or Basic?
4.0×10^{-7} M		
	1.5×10^{-6} M	
2.5×10^{-8} M		
	3.0×10^{-9} M	

Section 16.4 – The pH Scale

pH is defined as the negative logarithm (in base 10) of the concentration of H^+ (or H_3O^+).

$$pH = -\log[H^+] \qquad \text{or} \qquad pH = -\log[H_3O^+]$$

For example, the pH of a solution in which $[H^+] = 1.0 \times 10^{-7} = 7.00$

Only the numbers to the right of the decimal are the significant figures in a logarithm. For example, when the value of $[H^+]$ has two significant figures, the pH should have two decimal places.

(a) As the $[H^+]$ increases in a solution, the pH will _____________________.

(b) In chemistry, we use the convention that the "negative log" of some quantity is labeled p(quantity). Therefore the concentration of hydroxide ions in solution is expressed in terms of the ________. Similarly, $pK_w = -\log(K_w) =$ __________ at 25°C

You should also know that pH + pOH = __________ at 25°C

(c) Fill in the table below with the missing information.

$[H^+]$	pH	$[OH^-]$	pOH	Acidic or Basic?
2.5×10^{-5} *M*				
	7.92			
		6.8×10^{-4} *M*		
			11.16	

In the laboratory, pH can be determined with a pH meter, which is an electronic device that measures pH based on small voltages present in solution.

Acid-base indicators can be used to estimate the pH of a solution. The color of an acid-base indicator normally changes from one color to another over a certain pH range. The pH of a solution can be estimated by the color of various indicators.

(d) Use Figure 16.7 on page 664 to estimate the approximate pH of each solution.

Solution	Methyl orange	Methyl red	Bromthymol blue	Phenol-phthalein	Alizarin yellow R	Approximate pH
#1	orange	red	yellow	colorless	yellow	
#2	yellow	orange	yellow	colorless	yellow	
#3	yellow	yellow	blue	colorless	yellow	
#4	yellow	yellow	blue	pink	orange	

Section 16.5 – Strong Acids and Bases

$$HNO_3(aq) \quad + \quad H_2O(l) \quad \longrightarrow \quad H_3O^+(aq) \quad + \quad NO_3^-(aq)$$

(a) Explain why double arrows in opposite directions are not used in the reaction shown above.

(b) Write the reaction that shows how chloric acid behaves in water.

(c) With strong acids, the concentration of H^+ in solution the same as the concentration of the acid itself. (This is not the case with weak acids, as we will see in Section 16.6) Calculate the pH for each of the following concentrations of hydrochloric acid. Remember that if the concentration of $[H_3O^+]$ has two sig figs, the pH will have 2 decimal places.

Concentration of HCl	pH
0.50 *M*	
0.0075 *M*	
3.4×10^{-6} *M*	
1.5×10^{-8} *M*	

(d) The solution in the last row of the table in part (c) was very dilute. Did you notice anything strange about the calculated pH value? Is this value the correct pH of the solution? If not, explain what the pH of this very dilute acid solution should be and why.

(e) Calculate the concentration of nitric acid for each of the following solutions. Remember that if a pH has 2 decimal places, the concentration of $[H_3O^+]$ will have two sig figs.

Concentration of HNO_3	pH
	0.72
	2.04
	4.56
	6.14

The most common strong bases are the hydroxide compounds of the alkali metals, such as NaOH and KOH. Other strong bases include hydroxide compounds of the heavier alkaline earth metals, such as $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$.

(f) Fill in the missing information in the table below. Pay attention to the concentration of hydroxide in the last row of the table. $[OH^-]$ is <u>not</u> equal to 0.0050 *M* in 0.0050 *M* $Ca(OH)_2$.

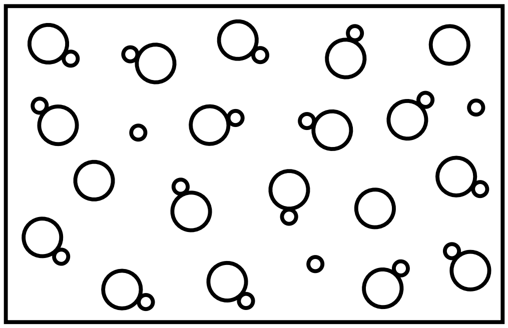
Solution	$[OH^-]$	pOH	pH
0.25 *M* NaOH			
0.0050 *M* KOH			
0.0050 *M* $Ca(OH)_2$			

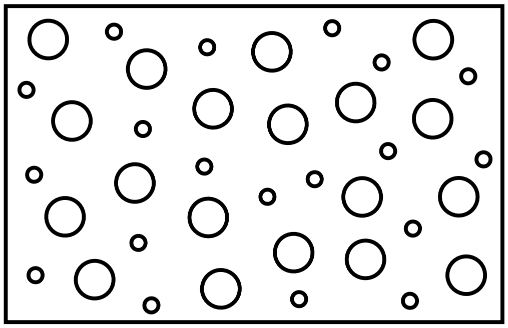
(g) Fill in the missing information in the tables below. Remember that something extra should be done to convert from $[OH^-]$ into concentration of $Sr(OH)_2$.

pH	pOH	Concentration of NaOH
10.23		
12.34		

pH	pOH	Concentration of $Sr(OH)_2$
10.23		
12.34		

<u>Section 16.6 – Weak Acids</u>





(a) Which diagram shown above best represents a weak acid?

(b) If we represent a generic weak acid as HA, write the equation for the ionization of HA in water.

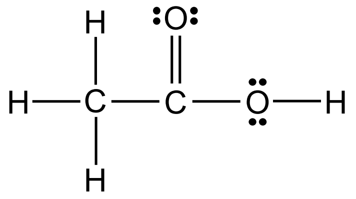
(c) Explain why double arrows in opposite directions should be used in the reaction you wrote in part (b).

(d) Write the equilibrium-constant expression for the ionization of a weak acid, HA.
K_a is called the acid-dissociation constant.

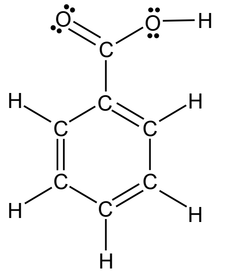
(e) Which of these two substances is a stronger acid? Justify your answer.

nitrous acid, HNO_2 ($K_a = 4.5 \times 10^{-4}$)   hydrocyanic acid, HCN ($K_a = 4.9 \times 10^{-10}$)

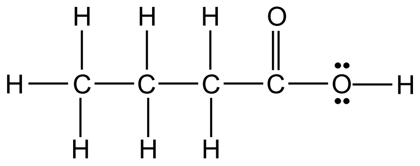
(f) Many weak acids contain a carboxylic acid group ($-CO_2H$).
Circle the acidic hydrogen atom in each of the following structural formulas.



acetic (ethanoic) acid

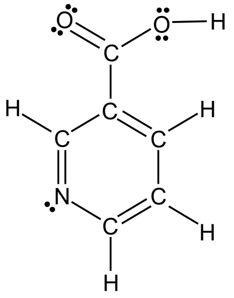


benzoic acid



butanoic acid

If you are given the concentration of a weak acid and the pH of the acid, it is possible to calculate the value of K_a.



(g) Nicotinic acid, also known as niacin or vitamin B_3, has the structural formula shown at right. Its formula can be written as $HC_6H_4NO_2$

(i) Write the equation for the dissociation of $HC_6H_4NO_2$ in water.

(ii) Write the acid-dissociation constant expression for nicotinic acid, $HC_6H_4NO_2$.

(iii) A 0.020 *M* solution of nicotinic acid has a pH of 3.26. Calculate the concentration of $[H^+]$ in a 0.020 *M* solution of this acid.

(iv) Use an ICE table similar to the one used in Sample Exercise 16.10 on page 668 to determine the concentrations of $HC_6H_4NO_2$, H^+, and $C_6H_4NO_2^-$ in a 0.020 *M* solution of nicotinic acid.

(v) Use the data from the final row of the ICE table to calculate the K_a for nicotinic acid.

(h) Percent ionization is defined by Equations 16.26 and 16.27 on page 669. Use the data from part (g) to calculate the percent ionization in a 0.020 *M* solution of nicotinic acid.

If you are given the concentration of a weak acid and the K_a value of the acid, it is possible to calculate the pH of the acid solution.

(i) Hypochlorous acid has the chemical formula HOCl.

(i) Write the equation for the dissociation of hypochlorous acid in water.

(ii) Write the acid-dissociation constant expression for hypochlorous acid.

(iii) The K_a for hypochlorous acid is 3.0×10^{-8}. Use an ICE table similar to the ones used on pages 670–671 to calculate the concentration of H^+ in a 0.020 *M* solution of hypochlorous acid. You should also calculate the pH of this solution.

As a general rule, if the percent ionization is less than 5% of the initial concentration of acid, then we can make that simplifying assumption that allows us to avoid the quadratic formula. **Read the information on the bottom half of page 670 (beginning with the phrase, "This expression leads to a quadratic…")** This section discusses the assumption and how to check its validity after you have solved for x.

(j) Calculate the percent ionization in a 0.020 *M* solution of hypochlorous acid.

(k) Compare the pH of a 0.020 M solution of nicotinic acid and the pH of a 0.020 M solution of hypochlorous acid. Which of these two acids is a stronger acid? Justify your answer based on the pH values, not based on their K_a values.

(l) The _____________ the K_a value is for an acid, the stronger the acid.

(m) Suppose that two different acids have the same concentration. The stronger acid is the one that has a _______________ pH.

(n) The value of K_a for acetic acid, CH_3CO_2H is equal to 1.8×10^{-5}.
Calculate [H^+], the pH, and the percent ionization for each of the following solutions.

Concentration of CH_3CO_2H	[H^+]	pH	% ionization
0.10 *M*			
0.010 *M*			
0.0010 *M*			

The trend observed in part (n) seems a little confusing. Why would the percent ionization for a weak acid *increase* as the concentration of the acid *decreases*? This trend is shown in Figure 16.11 on page 672, and it can be explained by using LeChatelier's principle.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

When a solution is diluted, the concentration of the dissolved particles decreases. In an acid dissociation equilibrium, there are more particles on the right side of the equation than on the left side. Therefore, the dilution of a weak acid causes the equilibrium to shift in the direction of the larger number of particles (toward the product side). This shift helps to counteract the effect of decreasing concentration of particles. Diluting a weak acid will increase its percent ionization.

(o) A monoprotic acid has only one ionizable H atom. Acids such as $H_2C_2O_4$ or H_3PO_4 have more than one ionizable H atom, so they are known as ________________________ acids.

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^- \qquad K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \qquad K_{a2} = 6.4 \times 10^{-8}$$

Note that K_{a2} (the equilibrium constant for the 2nd ionization step) is much smaller than K_{a1} (the equilibrium constant for the 1st ionization step.) This trend is typical for polyprotic acids. It is easier to remove the first H^+ ion than it is to remove the second H^+ ion. The explanation is as follows. The first H^+ ion is removed from a *neutral* molecule. The second H^+ ion is more difficult to remove because it is removed from an anion with a *negative* charge. There is greater attraction between the H^+ ion and the negatively charged anion. If there are three ionizable protons in the acid molecule, then K_{a3} will be even smaller than K_{a2}.

(p) As we have just seen, K_{a1} is usually much ______________ than K_{a2} (or K_{a3}.) Therefore, when calculating the pH of a polyprotic acid, we can usually treat the acid as if it were monoprotic. This allows us to focus on the ________ ionization step as the only significant source of H^+ ions in the solution.

(q) Sulfurous acid has the formula H_2SO_3. The K_a values for sulfurous acid can be found in Table 16.3 on page 674.

(i) Calculate the pH of a 0.10 *M* solution of sulfurous acid.

(ii) Calculate the concentration of the sulfite ion, SO_3^{2-}, in a 0.10 *M* solution of sulfurous acid.

As you can see from the answers to part (q), the 2nd ionization step for a diprotic acid occurs to a much smaller extent than the 1st ionization step does.

Section 16.7 – Weak Bases

(a) If we represent a generic weak base as B, write the equation for the ionization of B in water.

(b) Write the equilibrium-constant expression for the ionization of a weak base, B.
K_b is called the base-dissociation constant.

(c) Which of these two substances is a stronger base? Justify your answer.

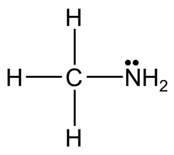
pyridine, C_5H_5N ($K_b = 1.7 \times 10^{-9}$)   methylamine, CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$)

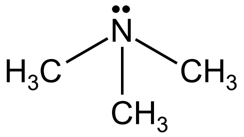
There are two categories of weak bases:

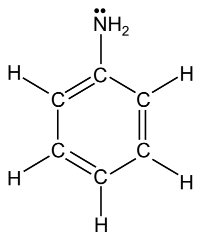
1) neutral molecules with an atom that has a lone pair of electrons that can accept H^+

2) anions that represent the conjugate base of a weak acid

(d) _________________ are organic compounds that contain a nitrogen atom with a lone pair of electrons capable of accepting H^+. Examples include the following compounds.
Circle the compound that represents the strongest base among these three.


methylamine
($K_b = 4.4 \times 10^{-4}$)


trimethylamine
($K_b = 6.4 \times 10^{-5}$)


aniline
($K_b = 4.3 \times 10^{-10}$)

(e) The ________________________ ion is one example of a basic anion. It is derived from

hypochlorous acid. The formula of this ion is ______________. Its K_b value is 3.3×10^{-7}.

(f) Another example of a basic anion is the _____________________ ion, which is derived from

hydrocyanic acid. Its K_b value is 2.0×10^{-5}.

If you are given the concentration of a weak base and the pH of the base, it is possible to calculate the value of K_b.

(g) A 0.25 *M* solution of ammonia has a pH of 11.33.

(i) What is the pOH of this solution? ____________

(ii) What is the concentration of hydroxide in this solution? ___________

(iii) What is the concentration of ammonium in this solution? __________

(iv) The concentration of ammonia is 0.25 *M*. Using this number and the answers to (ii) and (iii), plug these values into the K_b expression for NH_3. Calculate K_b for ammonia.

If you are given the concentration of a weak base and the K_b value of the base, it is possible to calculate the pH of the base solution.

(h) A solution of ammonia has a concentration of 0.050 *M*. Calculate the $[OH^-]$, pH, and percent ionization for this solution.

(i) A 1.00 L solution of sodium hypochlorite, NaOCl, has a pH of 9.50. Calculate each of the following quantities. ($K_b = 3.3 \times 10^{-7}$)

pOH　　$[OH^-]$　　$[HOCl]$　　$[OCl^-]$　　mass of NaOCl in the solution.

Section 16.8 – Relationship Between K_a and K_b

(a) Fill in the missing information in the table below.

		Equilibrium-Constant Expression
Dissociation of a weak acid, HA:	$HA \rightleftharpoons H^+ + A^-$	
Reaction of the conjugate base A^- with water:	$A^- + H_2O \rightleftharpoons HA + OH^-$	
The two reactions added together:		

(b) Write Equation 16.40 on page 679: ________________________

(c) Write Equation 16.41 on page 680: ________________________

(d) Calculate the pK_a value for each of the following acids:

Acetic acid, CH_3CO_2H (1.8×10^{-5})　　Hypochlorous acid, HOCl (3.0×10^{-8})

pK_a = ____________　　pK_a = ____________

(e) The lower the pK_a value is, the __________________ the acid is.

(f) Calculate the K_b value for each of the following bases:

Acetate, $CH_3CO_2^-$ Hypochlorite, ClO^-

K_b = ____________ K_b = ____________

(g) Describe the relationship between the K_a of an acid and the K_b of its conjugate base.

Section 16.9 – Acid-Base Properties of Salt Solutions

A solution of a salt can be classified as acidic or basic. When an anion reacts with water to generate H^+(*aq*) or OH^-(*aq*), this reaction is often called hydrolysis.

Consider the anions of these six strong acids that you memorized in Section 16.2.

Cl^- Br^- I^- NO_3^- ClO_3^- ClO_4^-

(a) Do these six anions act as strong bases in solution? _______

Do they act as weak bases in solution? ____________________

How do these ions affect the pH of a solution? ____________________________________

These six ions act as __________________ ions in acid-base reactions.

(b) Acetic acid (CH_3CO_2H) is a weak acid. Write an equation for the hydrolysis of the acetate ion.

(c) Based on the equation in part (b), sodium acetate (CH_3CO_2Na) behaves as ______________.

A solution of sodium acetate has a pH that is (less than more than) 7.00

Reaction #1: $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ $K_a = 4.2 \times 10^{-13}$

Reaction #2: $HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ $K_b = 1.6 \times 10^{-7}$

(d) In Reaction #1, the hydrogen phosphate ion, HPO_4^{2-} behaves as ____________.

In Reaction #2, HPO_4^{2-} behaves as _____________.

(e) Will a solution of Na_2HPO_4 be acidic or basic? _______________ Justify your prediction.

(f) Write an equation to show how the NH_4^+ ion behaves in water.

(f) The K_b of ammonia is equal to 1.8×10^{-5}. Calculate the K_a for the ammonium ion.

(g) How do the ions Li^+, Na^+, K^+, Ca^{2+} Sr^{2+} and Ba^{2+} affect the pH of an aqueous solution?

(h) According to Figure 16.16 on page 683, how can the Fe^{3+} ion behave as an acid?

The following is a summary of the acid-base properties of salt solutions.

If the cation is…	Examples include the following ions	…and the anion is…	Examples include the following ions	…the salt will be…
neutral	Group 1 cations or heavier members of Group 2 (Ca^{2+}, Sr^{2+}, Ba^{2+})	neutral	conjugate base of a strong acid (Cl^-, Br^-, I^-, NO_3^-, ClO_3^-, ClO_4^-)	neutral
neutral	Group 1 cations or heavier members of Group 2 (Ca^{2+}, Sr^{2+}, Ba^{2+})	basic	conjugate base of a weak acid (F^-, ClO^-, $C_2H_3O_2^-$, CO_3^{2-})	basic
acidic	conjugate acid of a weak base (NH_4^+) or a small, highly charged metal ion (Al^{3+}, Cr^{3+}, Fe^{3+})	neutral	conjugate base of a strong acid (Cl^-, Br^-, I^-, NO_3^-, ClO_3^-, ClO_4^-)	acidic

There is a fourth possibility to consider. A salt may contain both an acidic cation and basic anion. In this case, the behavior of the salt in solution depends on the relative strength of these two ions.

If K_a for the acidic cation is greater than K_b for the basic anion, the salt should be acidic.

If K_b for the basic anion is greater than K_a for the acidic cation, the salt should be basic.

Section 16.10 – Acid-Base Behavior and Chemical Structure

(a) The strength of the H–X bond tends to __________________ as element X increases in size.

(b) The higher the bond energy, the _______________________ it is for that bond to be broken.

Bond (H–X)	H–F	H–Cl	H–Br	H–I
Bond Energy (kJ/mol)	567	431	366	299

(c) How does the data in the table above help to explain the difference in acid strength between hydrofluoric acid (HF) and hydrochloric acid (HCl)?

(d) Moving left to right across a period, electronegativity tends to ___________________.

Moving top to bottom down a group, electronegativity tends to ___________________.

(e) Which bond is more polar, H–O or H–F? How does this difference in bond polarity help to explain the difference in acid strength between hydrofluoric acid (HF) and water?

(f) Which atom is more electronegative, chlorine or iodine? How does this difference in electronegativity explain the difference in acid strength between hypochlorous acid ($HOCl$) and hypoiodous acid (HOI)?

(g) Explain why chloric acid ($HClO_3$) is a stronger acid than hypochlorous acid ($HClO$).

(h) What is a carboxyl group? Explain how resonance helps to explain the stability of the conjugate base in a carboxylic acid.

Section 16.11 – Lewis Acids and Bases

This concept has been de-emphasized in the AP Chemistry curriculum and will not be featured on the AP Exam.