

# 13

## BIG IDEA 6: APPLICATIONS OF EQUILIBRIA: PROTON TRANSFER AND SOLUBILITY

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### Big Idea 6

Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external perturbations.

Concepts from the last chapter will be applied in this section covering the equilibria of weak acids, weak bases, and salts. In addition, acid-base theories and properties of acids will be reviewed. Calculations involved in acid-base titrations, preparation of buffers, and salt hydrolysis will be demonstrated. In addition, you will apply basic equilibrium concepts involving solids dissolving to form aqueous solutions.

You should be able to

- Understand the Brønsted–Lowry acid–base theory.
- Identify strong acids and bases and calculate their pH's.
- Calculate the pH of a weak acid or base.
- Calculate the concentration of a strong or weak acid or base from its pH.

- Calculate the pH and ion concentrations in a polyprotic acid.
- Predict the pH of a salt from its formula and then calculate the pH of the salt.
- Identify the components of a buffer and perform calculations involving the preparation of a buffer and the addition of strong acid or strong base to a buffer.
- Perform calculations involving strong acid–strong base titrations as well as weak acid–strong base and weak base–strong acid calculations.
- Be familiar with titration curves and selection of an acid–base indicator.
- Write balanced equations for the dissolution of a salt and its corresponding solubility product expression.
- Predict the relative solubilities of salts which dissolve to give the same number of ions from their  $K_{sp}$  values.
- Calculate the  $K_{sp}$  value from the solubility of a salt and also calculate the solubility of the salt in units of mol/L or g/L from the given  $K_{sp}$  value.
- Predict the effect of a common ion on the solubility of a salt and perform calculations.
- Perform calculations to predict if a precipitate will form when two solutions are mixed.

### AP Tip

Be systematic. All solution equilibrium problems have the same basic features—a ratio of product concentrations and reactant concentrations raised to their stoichiometric coefficients. Remember that pure substances are not involved in equilibrium calculations.

## ACID–BASE THEORY

### BRØNSTED–LOWRY

(Chemistry 8th ed. pages 639–642/9th ed. pages 653–656)

The Brønsted–Lowry theory says that an acid is a proton ( $H^+$ ) donor and a base is a proton acceptor.

In the reaction below,  $HNO_3$  transfers a proton to  $H_2O$  forming  $H_3O^+$ , the hydronium ion.  $H_3O^+$  is the conjugate acid of  $H_2O$  and  $NO_3^-$  is the conjugate base of  $HNO_3$ . The formulas in a conjugate acid–base pair differ by one  $H^+$ .



**EXAMPLE:** Give the formulas for the conjugate base of  $H_2SO_4$  and the conjugate acid of  $CH_3NH_2$ .

**SOLUTION:**  $HSO_4^-$  is the conjugate base of  $H_2SO_4$ .

$\text{CH}_3\text{NH}_3^+$  is the conjugate acid of  $\text{CH}_3\text{NH}_2$ .

Note that each conjugate acid–base pair differs by 1  $\text{H}^+$ :



## ACID AND BASE STRENGTH

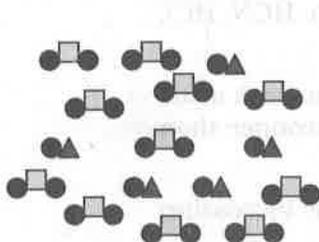
(Chemistry 8th ed. pages 642–645, 661–662/9th ed. pages 656–659, 675–676)

The names and formulas of the six strong acids must be memorized. The six strong acids are  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$ .

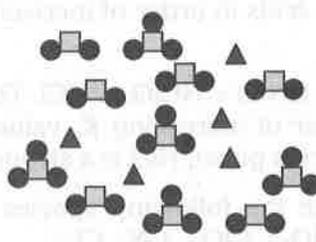
If an acid is not one of the six in the list, then for purposes of the AP exam, you can assume it is a weak acid. Common weak acids include carboxylic acids and most oxyacids. Several factors affect the magnitude of  $K_a$  of weak acids: bond strength, solvation, and electronegativity of the atom bonded to the proton that will ionize.

A particulate model is especially useful for understanding the differences between strong and weak acids.

Dissociation of a Strong Acid

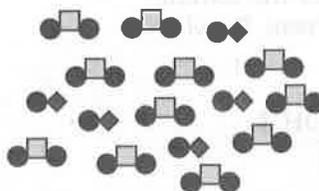
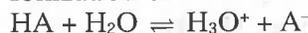


before dissociation

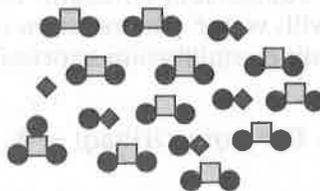


after dissociation

Ionization of a Weak Acid

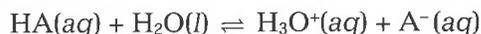


before ionization



after ionization

Weak acids exist in equilibrium with their ions in aqueous solution. The equilibrium constant,  $K_a$ , measures the extent to which the acid dissociates in water:



The equilibrium expression for the reaction is

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

A table of  $K_a$  values for monoprotic acids, containing one acidic hydrogen, appears in the appendix of *Chemistry* (8th ed. page A22/9th ed. page A22) and many other textbooks and is worth studying. The larger the  $K_a$  value, the stronger the acid.

Comparison of Strong and Weak Acids				
Type of acid, HA	Reversibility of reaction	$K_a$ value	$\text{p}K_a$ Value	Ions existing when acid, HA, dissociates in $\text{H}_2\text{O}$
Strong	not reversible	very large	negative	$\text{H}_3\text{O}^+$ and $\text{A}^-$ , only. No HA present.
Weak	reversible	small	positive Smaller values indicate equilibrium lies more toward products.	$\text{H}_3\text{O}^+$ , $\text{A}^-$ , and HA

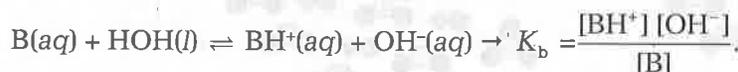
**EXAMPLE:** List the acids in order of increasing strength: HCN, HCl,  $\text{HClO}_2$ ,  $\text{HNO}_2$ .

**SOLUTION:**  $\text{HCN} < \text{HNO}_2 < \text{HClO}_2 < \text{HCl}$ . The first three weak acids are listed in order of increasing  $K_a$  values. HCl is stronger than all of the weak acids given. HCl is a strong acid.

**EXAMPLE:** Arrange the following species in order of increasing base strength:  $\text{NO}_2^-$ ,  $\text{ClO}_2^-$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ .

**SOLUTION:**  $\text{Cl}^- < \text{ClO}_2^- < \text{NO}_2^- < \text{CN}^-$ . The bases are listed in reverse order of their conjugate acids in the previous example because the stronger the acid, the weaker its conjugate base.

Strong bases include group 1A and 2A hydroxides such as NaOH. Weak bases include ammonia, amines, and pyridines, and other nitrogenous bases. The equilibrium constant,  $K_b$ , measures the extent to which a base reacts with water. The reaction of a weak base, B, with water and its corresponding equilibrium expression is



The acid and base equilibrium constants,  $K_a$  and  $K_b$  are related to each other through the equilibrium constant of water,  $K_w$ .

$$K_w = K_a K_b$$

**AP Tip**

Writing the reaction for base ionization can be tricky. Always remember to react the base with water. For example, the base reacts with water to produce hydroxide ions and accepts a hydrogen ion to become protonated. Remember to check the charges of the reactants and products and be sure that the sums of the charges on both sides of the reaction are equal.

**THE EFFECT OF STRUCTURE ON ACID–BASE PROPERTIES**

(Chemistry 8th ed. pages 667–678/9th ed. pages 681–693)

For binary acids, HX, the strength of the H–X bond and the polarity of the bond will determine the behavior of the acid. The polarity of the bonds in hydrogen halides become less polar going down a group. The very strong H–F bond is what makes it a weak acid: F<sup>-</sup> has a very high attraction for H<sup>+</sup> so a great deal of energy is needed to break the bond. The rest of the hydrogen halides are strong acids: HI > HBr > HCl.

For a given series of oxyacids such as HClO<sub>4</sub>, HClO<sub>3</sub>, HClO<sub>2</sub>, and HClO, the acid strength increases with increasing number of oxygen atoms attached to the central atom. HClO<sub>4</sub> is a strong acid. The remaining oxyacids are listed in order of decreasing strength (decreasing number of oxygen atoms). The O–H bond becomes more polarized and weakened due to the electron density drawn toward the highly electronegative oxygen atoms.

**CALCULATING THE pH OF STRONG ACIDS AND BASES**

(Chemistry 8th ed. pages 650–651, 662–663/9th ed. pages 665–666, 676–677)

The pH of a strong acid can be calculated directly from the hydronium (or hydrogen) ion concentration,

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

[H<sub>3</sub>O<sup>+</sup>], the molar concentration of the hydronium ion, is obtained from the molarity of the acid.

**EXAMPLE:** Calculate the pH of 0.025 M HCl.

**SOLUTION:** The pH equals 1.60;  $-\log (0.025) = 1.60$ . Recall that in strong acids the concentration of the acid equals [H<sub>3</sub>O<sup>+</sup>].

The pH of a strong base can be calculated from its hydroxide ion concentration.

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14.00$$

The concentration of a strong acid or strong base can be determined from the solution's pH.

**EXAMPLE:** The pH of a  $\text{Sr}(\text{OH})_2$  solution is 13.50. Calculate the concentration of  $\text{Sr}(\text{OH})_2$ .

**SOLUTION:**  $\text{pOH} = 14 - \text{pH} = 14 - 13.50 = 0.50$

$[\text{OH}^-] = 10^{(-\text{pOH})}$ ;  $10^{(-0.50)} = 0.32 \text{ M OH}^-$

$\frac{0.32 \text{ mol OH}^-}{1 \text{ L}} \times \frac{1 \text{ mol Sr}(\text{OH})_2}{2 \text{ mol OH}^-} = 0.16 \text{ M Sr}(\text{OH})_2$

### AP Tip

The number of significant figures in a pH measurement is equal to the number of decimal places in the pH. For example, a pH of 1.70 has 2 significant figures.

## CALCULATING THE pH OF WEAK ACIDS

(Chemistry 8th ed. pages 651–656/9th ed. pages 666–671)

The pH of a weak acid cannot be calculated directly from the concentration of the acid since all of the acid does not dissociate to form  $\text{H}_3\text{O}^+$ . The equilibrium reaction of the acid must be considered.

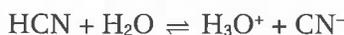
### AP Tip

Always follow these steps when performing calculations involving the dissociation of weak acids or weak bases.

1. Write the reaction of the acid or base with water. (Use Brønsted–Lowry acid–base theory and check charges.)
2. Set up an ICE chart.
3. Write the equilibrium expression in terms of reactant and product concentrations (without numbers).
4. Solve for  $x$ , using the method of approximation. Test approximation. Solve a quadratic equation if necessary.
5. Solve for pH. (Be careful with base equilibria:  $x = \text{OH}^-$ . You need to find pOH and then pH.)
6. Always remember that for weak acids and bases, at equilibrium,  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ .

**EXAMPLE:** Calculate the pH of 0.025 M HCN.

**SOLUTION:** First, write the reaction of the acid with water. Use the Brønsted–Lowry theory to help you write the products. Check that you have the correct charges on the products.



Second, set up an ICE chart as you did in the previous chapter for equilibrium problems.

	HCN +	H <sub>2</sub> O ⇌	H <sub>3</sub> O <sup>+</sup> +	CN <sup>-</sup>
I	0.025		0	0
C	-x		+x	+x
E	0.025 - x		x	x

Third, write the equilibrium expression for  $K_a$  in the same manner as you did in the last chapter. Plug in the values from the equilibrium line of the ICE chart.

$$K_a = 6.2 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}; \frac{x^2}{(0.025 - x)} \approx \frac{x^2}{0.025}$$

If  $x$  is very small compared to the concentration of the acid you are subtracting it from, then you can assume  $[\text{HA} - x]$  is approximately equal to  $[\text{HA}]$ . One way to determine if this approximation is valid is to compare the magnitude of  $K$  to  $[\text{HA}]$ ; if  $[\text{HA}]$  is greater than  $K$  by a factor of  $10^3$  or more then  $x$  can be safely ignored. You can always assume that  $x$  is small and then check the value of  $x$  you calculate to see if  $[\text{HA} - x]$  is within 5% of  $[\text{HA}]$ .

Fourth, solve for  $x$  which equals  $\text{H}_3\text{O}^+$ .

$$x^2 = (6.2 \times 10^{-10})(0.025)$$

$$x = [\text{H}_3\text{O}^+] = 3.9 \times 10^{-6} \text{ M}$$

Finally calculate the pH from the value of  $x$ , the  $\text{H}_3\text{O}^+$  concentration.

$$\text{pH} = -\log(3.9 \times 10^{-6}) = 5.40$$

As you can see, acid strength and concentration both play a role in the pH of a solution. At the same concentration, the strong acid was pH 1.60 while the weak acid was pH 5.40. The difference is due to the higher  $[\text{H}_3\text{O}^+]$  in the strong acid.

## CALCULATING THE PERCENT IONIZATION

(Chemistry 8th ed. pages 657–660/9th ed. pages 672–675)

The percent ionization of an acid (or a base) is the amount of the acid,  $\text{HA}$ , which has ionized,  $x$ , divided by the acid's initial concentration,  $[\text{HA}]_0$ , multiplied by 100.

$$\% \text{ ionization} = \frac{x}{[\text{HA}]_0} \times 100$$

When making assumptions in an equilibrium calculation, it is best to test the assumption by making sure that the percent dissociation is less than or equal to 5%. The test for the assumption is the same as the calculation for the percent dissociation.

**EXAMPLE:** The percent ionization of an acid,  $\text{HA}$ , which is 0.100 M is 2.5%. Calculate the  $K_a$  of the acid.

SOLUTION:  $x/0.100 M \times 100 = 2.5\%$ ;  $x = 2.5 \times 10^{-3} M$

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

$$K_a = \frac{(2.5 \times 10^{-3})^2}{0.100 - 2.5 \times 10^{-3}} = 6.4 \times 10^{-5}$$

## CALCULATING THE pH OF WEAK BASES

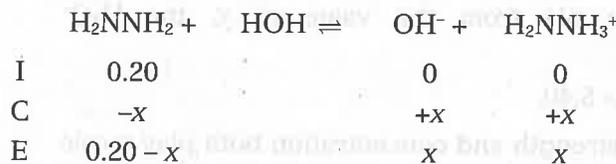
(Chemistry 8th ed. pages 662–666/9th ed. pages 675–680)

The calculations involving weak base equilibria are similar to the weak acid equilibria problems except that the equation is written for a base reacting with water and the calculation initially involves finding  $[\text{OH}^-]$ . You will need to find the pOH and then the pH.  $\text{p}K_b$  values can be used to determine the position of equilibrium: smaller values indicate equilibrium favors products.

EXAMPLE: The pH of a 0.20 M solution of  $\text{H}_2\text{NNH}_2$  is 11.38. Calculate  $K_b$  for  $\text{H}_2\text{NNH}_2$ .

Write the reaction with water. Bases accept  $\text{H}^+$ . Watch charges! One hint to help in writing the reaction is that the pH is 11.38. The basic pH indicates that  $\text{OH}^-$  must be one of the products.

Fill out the ICE chart under the reaction.



You are given the pH, but x equals  $[\text{OH}^-]$ .

Find pOH;  $\text{pH} + \text{pOH} = 14.00$ ;  $\text{pOH} = 14.00 - 11.38 = 2.62$

$\text{pOH} = -\log [\text{OH}^-]$ ; Find  $[\text{OH}^-] = 10^{(-\text{pOH})}$ ,

$$10^{(-2.62)} = 2.4 \times 10^{-3} M$$

Plug this value of x into the  $K_b$  expression:

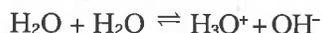
$$K_b = \frac{[\text{OH}^-][\text{H}_2\text{NNH}_3^+]}{[\text{H}_2\text{NNH}_2]} = \frac{x^2}{(0.20 - x)}$$

$$K_b = \frac{(2.4 \times 10^{-3})^2}{0.20} = 2.9 \times 10^{-5}$$

## CONJUGATE ACID–BASE PAIRS

(Chemistry 8th ed. page 645/9th ed. page 659)

Water is an amphoteric substance; it can act as an acid or a base according to the reaction



The equilibrium expression for this reaction is

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

where  $K_w$  is the equilibrium constant for the ionization of water. Water is neutral whenever  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ . At  $25^\circ\text{C}$   $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ , but since this is an endothermic equilibrium reaction, the concentrations are temperature dependent.

This relationship can be expressed as

$$\text{p}K_w = \text{pH} + \text{pOH}$$

Since  $\text{p}K_w$  is 14.00 at  $25^\circ\text{C}$ , the equation is often written as

$$14.00 = \text{pH} + \text{pOH}$$

The equation can be generalized for any acid–base pair in aqueous solution at  $25^\circ\text{C}$  as

$$14.00 = \text{p}K_a + \text{p}K_b$$

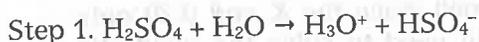
## POLYPROTIC ACIDS

(Chemistry 8th ed. pages 666–671/9th ed. pages 681–686)

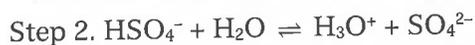
Polyprotic acids can donate more than one proton,  $\text{H}^+$ , and dissociate by losing 1  $\text{H}^+$  at a time. Sulfuric acid,  $\text{H}_2\text{SO}_4$  is the only strong acid that is polyprotic.

**EXAMPLE:** Calculate the pH of a 0.10 M solution of  $\text{H}_2\text{SO}_4$ .  $K_{a1}$  = very large;  $K_{a2} = 1.2 \times 10^{-2}$ .

**SOLUTION:** The dissociation of  $\text{H}_2\text{SO}_4$  occurs in a stepwise fashion where the first step goes to completion and the second step is an equilibrium.



$$[\text{H}_2\text{SO}_4] = [\text{H}_3\text{O}^+] = [\text{HSO}_4^-] = 0.50 \text{ M}$$



	$\text{HSO}_4^-$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{SO}_4^{2-}$
I	0.10				0.10		0
C	-x				+x		+x
E	0.10 - x				0.10 + x		x

Because  $K_a$  and the acid concentration are close to each other,  $x$  cannot be ignored and a quadratic equation must be solved to determine  $[\text{H}_3\text{O}^+]$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

$$1.2 \times 10^{-2} = \frac{(0.10 + x)(x)}{(0.10 - x)}$$

$$0 = x^2 + 0.112x - 1.2 \times 10^{-3}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.112 \pm \sqrt{0.112^2 - 4(1)(-1.2 \times 10^{-3})}}{2(1)}$$

$$x = 9.8 \times 10^{-3}$$

$$[\text{H}_3\text{O}^+] = 0.10 + 0.0098 \text{ M} = 0.11 \text{ M}$$

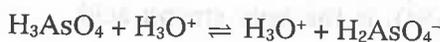
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.11) = 0.96$$

**EXAMPLE:** Calculate the  $[\text{H}_3\text{O}^+]$  of a 0.20 M solution of  $\text{H}_3\text{AsO}_4$ .

Also determine the concentrations of  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ .

For  $\text{H}_3\text{AsO}_4$ ,  $K_{a1} = 5 \times 10^{-3}$ ,  $K_{a2} = 8 \times 10^{-8}$ ,  $K_{a3} = 6 \times 10^{-10}$ .

	$\text{H}_3\text{AsO}_4$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{H}_2\text{AsO}_4^-$
I	0.20			0	0
C	-x			+x	+x
E	0.20 - x			x	x



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_4]}$$

$$5 \times 10^{-3} = \frac{x^2}{0.20 - x}$$

**Note:** You cannot assume  $x$  is small since the  $K$  and 0.20 only differ by a factor of  $10^2$ . You will need to solve the quadratic equation to solve for  $x$ .

$$x = 3 \times 10^{-2} \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{H}_2\text{AsO}_4^-] = 3 \times 10^{-2} \text{ M}$$

$$[\text{H}_3\text{AsO}_4] = 0.20 - 0.03 = 0.17 \text{ M}$$

Since  $K_{a3} \lll K_{a2} \lll K_{a1}$ , very little of  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  dissociates compared to  $\text{H}_3\text{AsO}_4$ , so  $[\text{H}_3\text{O}^+]$  and  $[\text{H}_2\text{AsO}_4^-]$  will not change very much by the  $K_{a2}$  dissociation, and we can use their concentrations to find the concentration of  $\text{HAsO}_4^{2-}$ .

	$\text{H}_2\text{AsO}_4^-$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{HAsO}_4^{2-}$
I	$3 \times 10^{-2}$			$3 \times 10^{-2}$	0
C	-x			+x	+x
E	$3 \times 10^{-2} - x$			$3 \times 10^{-2} + x$	x

$$K_{a2} = 8 \times 10^{-8} = \frac{(3 \times 10^{-2})[\text{HAsO}_4^{2-}]}{(3 \times 10^{-2})}$$

$[\text{HAsO}_4^{2-}] = 8 \times 10^{-8} \text{ M}$ ; the assumption that  $K_{a_2}$  does not contribute significantly to  $[\text{H}_3\text{O}^+]$  and  $[\text{H}_2\text{AsO}_4^-]$  is good.

Repeat the process to find  $[\text{AsO}_4^{3-}]$ .

	$\text{HAsO}_4^{2-} +$	$\text{H}_2\text{O} \rightleftharpoons$	$\text{H}_3\text{O}^+ +$	$\text{AsO}_4^{3-}$
I	$8 \times 10^{-8}$		$3 \times 10^{-2}$	0
C	$-x$		$+x$	$+x$
E	$8 \times 10^{-8} - x$		$3 \times 10^{-2} + x$	$x$

$$K_{a_3} = 6 \times 10^{-10} = \frac{(3 \times 10^{-2}) [\text{AsO}_4^{3-}]}{(8 \times 10^{-8})}$$

$[\text{AsO}_4^{3-}] = 2 \times 10^{-15} \text{ M}$ . Assumption that  $x$  is small is valid.

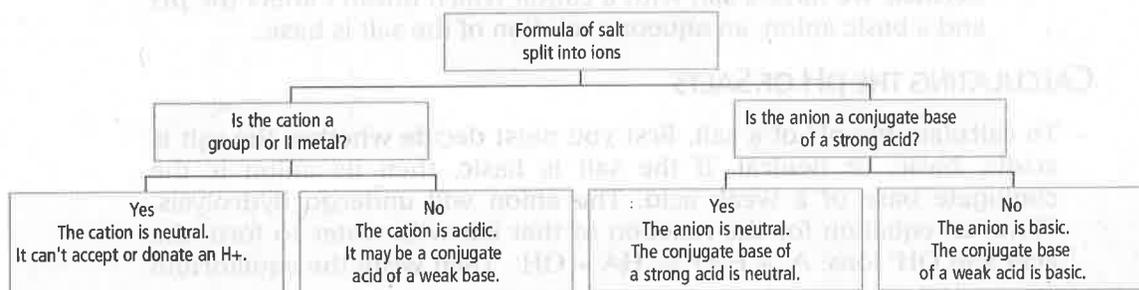
## ACID-BASE PROPERTIES OF SALTS

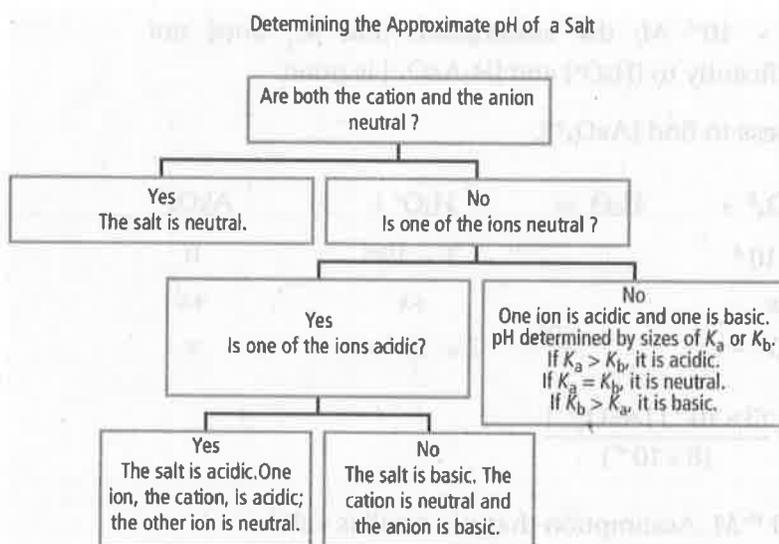
(Chemistry 8th ed. pages 671–677/9th ed. pages 686–691)

### PREDICTING THE pH OF SALTS

You may be asked to determine if a salt is acidic, basic, or neutral by looking at its chemical formula. This process involves two steps, as outlined in the flowcharts which follow. In the first flowchart, you determine the acidity or basicity of the individual ions. Then, using the second chart and the results from the first flowchart, you can determine if the salt is acidic, basic, or neutral.

Determining the Approximate pH of Ions in a Salt





**EXAMPLE:** Determine whether an aqueous solution of  $\text{KC}_2\text{H}_3\text{O}_2$  is acidic, basic, or neutral.

**SOLUTION:**  $\text{KCH}_3\text{O}_2$  is basic. Use the method of asking questions outlined above.

Split the salt into its cation,  $\text{K}^+$ , and its anion,  $\text{C}_2\text{H}_3\text{O}_2^-$ .

Is the cation a Group I metal? Yes; the cation does not affect the pH.

Is the anion a conjugate base of a strong acid? No;  $\text{C}_2\text{H}_3\text{O}_2^-$  is the conjugate base of a weak acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , which makes the solution basic.

Because we have a salt with a cation which doesn't affect the pH and a basic anion, an aqueous solution of the salt is basic.

## CALCULATING THE pH OF SALTS

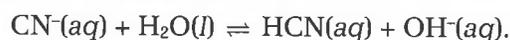
To calculate the pH of a salt, first you must decide whether the salt is acidic, basic, or neutral. If the salt is basic, then its anion is the conjugate base of a weak acid. The anion will undergo hydrolysis. Write an equation for the reaction of that ion with water to form the acid and  $\text{OH}^-$  ions:  $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ . Then write the equilibrium expression:

$$K_b = \frac{K_w}{K_a} = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

If the salt is basic, then the hydrolysis reaction will produce an acid.

**EXAMPLE:** Determine the pH of a 0.100 M aqueous solution of  $\text{NaCN}$ . The  $K_a$  for  $\text{HCN}$  is  $5.8 \times 10^{-10}$ .

**SOLUTION:** In aqueous solutions,  $\text{NaCN}$  ionizes completely into  $\text{Na}^+$  and  $\text{CN}^-$ . However, the cyanide ions ionize in water according to the following equation:



$\text{Na}^+$  ions do not affect the pH. Ions from Group IA and IIA never undergo hydrolysis because they are cations of strong bases. The equilibrium expression for the solution is

$$K_b = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]}$$

We need a value for  $K_b$ . Since we have  $K_a$  for HCN, we can calculate the value of  $K_b$  for  $\text{CN}^-$ .

$$K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{5.8 \times 10^{-10}}$$

$$K_b = 1.7 \times 10^{-5}$$

Constructing a table for filling in the available information, we get

	$\text{CN}^- +$	$\text{H}_2\text{O} \rightleftharpoons$	$\text{HCN} +$	$\text{OH}^-$
I	0.100		0	0
C	-x		+x	+x
E	$0.100 - x$		x	x

Since  $K$  is much smaller than 0.100, assume that  $0.100 - x \approx 0.100$ .

$$K_b = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]}; 1.7 \times 10^{-5} = \frac{x^2}{0.100}$$

Solving for  $x$ , we have

$$x = [\text{OH}^-] = 1.3 \times 10^{-3}$$

$$\text{pOH} = 2.89; \text{pH} = 14.00 - \text{pOH}$$

$$\text{pH} = 11.11$$

## BUFFERS

(Chemistry 8th ed. pages 701–713/9th ed. pages 715–727)

Buffers resist changes in pH when acids or bases are added. The components of a buffer are summarized in the next table.

Buffer	
Components	Examples
Similar concentrations of weak acid + salt containing the conjugate base	$\text{HCN}$ and $\text{NaCN}$
Similar concentrations of weak base + salt containing the conjugate acid	$\text{CH}_3\text{NH}_2$ and $\text{CH}_3\text{NH}_3\text{Cl}$
Excess weak acid + strong base	2 mol of $\text{HCN}$ + 1 mol $\text{NaOH}$ react to yield 1 mol $\text{HCN}$ and 1 mol $\text{NaCN}$
Excess weak base + strong acid	2 mol $\text{NH}_3$ + 1 mol $\text{HCl}$ react to yield 1 mol $\text{NH}_3$ and 1 mol $\text{NH}_4\text{Cl}$

Buffers cannot be made with strong acids or strong bases because their conjugate forms are extremely weak and the system is not in equilibrium; it has gone to completion.

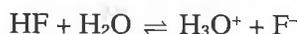
Buffer pH is related to the  $pK_a$  and the relative amounts of the acid and base forms. Buffer capacity is proportional to the actual concentrations of the acid and base forms. A buffer will maintain pH as long as both the acid and base forms are present.

### CALCULATING THE pH OF A BUFFER

The calculation to find the pH of a buffer is similar to all equilibrium calculations *except* there are now two initial concentrations, one for each part of the buffer pair.

**EXAMPLE:** Calculate the pH of a solution that is 0.60 M HF and 1.00 M KF.  $K_a$  for HF is  $7.2 \times 10^{-4}$ .

**SOLUTION:** First, write the reaction of the acid with water. (You are given  $K_a$ , and the buffer is a made of a weak acid and its conjugate base.)



Second, set up an ICE chart. Since KF is a soluble salt,  $[\text{F}^-] = [\text{KF}] = 1.00 \text{ M}$ .

	HF +	H <sub>2</sub> O ⇌	H <sub>3</sub> O <sup>+</sup> +	F <sup>-</sup>
I	0.60		0	1.00
C	-x		+x	+x
E	0.60 - x		x	1.00 + x

Third, write the equilibrium expression for  $K_a$ .

Plug in the values from the equilibrium line of the ICE chart. Check to see if  $x$  is small.

$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{x(1.00 - x)}{(0.60 - x)} = \frac{x(1.00)}{0.60}$$

Fourth, solve for  $x$  which equals  $\text{H}_3\text{O}^+$ .

$$K_a = 7.2 \times 10^{-4} = \frac{x(1.00)}{0.60}$$

$$x = [\text{H}_3\text{O}^+] = 4.3 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(4.3 \times 10^{-4}) = 3.36$$

An alternative method of solving a buffer problem is to use the Henderson-Hasselbalch equation

Henderson-Hasselbalch Equation

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{conjugate base}]}{[\text{weak acid}]} \right)$$

where  $\text{p}K_a = -\log K_a$ .

**EXAMPLE:** Repeat the example above with the Henderson-Hasselbalch equation.

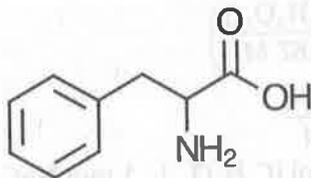
**SOLUTION:**  $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{F}^-]}{[\text{HF}]}\right)$

$$\text{pH} = -\log(7.2 \times 10^{-4}) + \log\left(\frac{1.00}{0.60}\right)$$

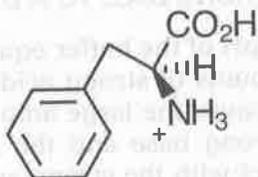
$$\text{pH} = 3.14 + 0.22 = 3.36$$

Comparing the pH and  $\text{p}K_a$  of a buffer can give a qualitative indication of the predominant species present. When  $\text{pH} = \text{p}K_a$ ,  $[\text{A}^-] = [\text{HA}]$ . When  $\text{pH} > \text{p}K_a$ ,  $[\text{A}^-] > [\text{HA}]$  and when  $\text{pH} < \text{p}K_a$ ,  $[\text{HA}] > [\text{A}^-]$ . Applications of this relationship include acid-base indicators and protonation of amino acids in polypeptides and proteins.

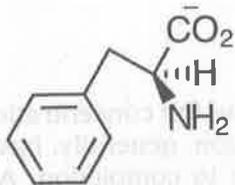
**EXAMPLE:** Identify the forms of phenylalanine in highest concentration at pH 2 and 10.  $\text{p}K_a = 2.58$  (acid), 9.24 (amine)



**SOLUTION:** pH 2 is less than the  $\text{p}K_a$ , so the amino group in phenylalanine will be fully protonated. It will attract the hydrogen from  $\text{H}_3\text{O}^+$  and will leave  $\text{H}_2\text{O}$  behind.



pH 10 is greater than the  $\text{p}K_a$  of the amine, so the molecule will be fully deprotonated—the hydrogen on the carboxylic acid group will be attracted to  $\text{OH}^-$  in the solution forming water.



### PREPARATION OF A BUFFER

A buffer can be made from a weak acid and a salt containing its conjugate base or from a weak base and a salt containing its conjugate acid.

**EXAMPLE:** Calculate the mass of  $\text{NaC}_2\text{H}_3\text{O}_2$  required to prepare a buffer of pH 4.55 when added to 0.500 L of 0.67 M acetic acid. (Assume no change in volume.)  $K_a = 1.8 \times 10^{-5}$  for  $\text{HC}_2\text{H}_3\text{O}_2$ .

**SOLUTION:** This problem can be solved using an ICE chart or by using the Henderson–Hasselbalch equation. Once  $[\text{C}_2\text{H}_3\text{O}_2^-]$  is calculated, stoichiometry is used to relate concentration to mass.

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$4.55 = 4.74 + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{0.67 \text{ M}} \right)$$

$$-0.19 = \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{0.67 \text{ M}} \right)$$

$$0.65 = \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{0.67 \text{ M}}$$

$$\text{mass NaC}_2\text{H}_3\text{O}_2 = \frac{0.44 \text{ mol } [\text{C}_2\text{H}_3\text{O}_2^-]}{\text{L}} \times \frac{1 \text{ mol NaC}_2\text{H}_3\text{O}_2}{1 \text{ mol } [\text{C}_2\text{H}_3\text{O}_2^-]} \times \frac{0.500 \text{ L} \times 82.0 \text{ g}}{1 \text{ mol NaC}_2\text{H}_3\text{O}_2}$$

$$\text{mass NaC}_2\text{H}_3\text{O}_2 = 1.8 \text{ g}$$

### ADDITION OF STRONG ACID AND STRONG BASE TO A BUFFER

When the  $[\text{A}^-]/[\text{HA}]$  ratio is 1, the pH of the buffer equals the  $\text{p}K_a$  of the weak acid. Addition of small amounts of strong acid or base will not significantly change this ratio because the large amount of weak acid is available to react with the strong base and the large amount of conjugate base is available to react with the strong acid. It is not until the  $[\text{A}^-]/[\text{HA}]$  ratio changes by a factor of 10 that the pH changes by 1 unit.

### TITRATION

(Chemistry 8th ed. pages 713–728/9th ed. pages 727–742)

A titration can be used to determine the concentration of an unknown solution. The neutralization reaction generally has  $K > 1$  so these reactions can be considered to go to completion. At the equivalence point, the moles of titrant and moles of analyte are present in stoichiometric ratios; neither one is in excess. Near the equivalence point the pH changes rapidly as fewer moles of analyte are present.

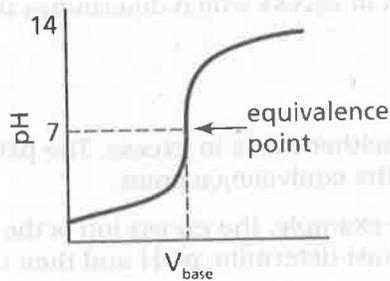
The table below summarizes the other types of problems involving acid–base titrations. Examples of each type of titration problem follow the table.

<b>Characteristics of Titrations</b>			
<b>Titrations</b>	<b>Before equivalence point</b>	<b>At equivalence point</b>	<b>After equivalence point</b>
Strong acid titrated with a strong base	Use excess $[\text{H}_3\text{O}^+]$ to calculate the pH $\text{pH} < 7$	$\text{pH} = 7$	Use excess $[\text{OH}^-]$ to calculate the pH $\text{pH} > 7$
Species in solution which affect the pH (in addition to $\text{H}_2\text{O}$ )	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	$\text{OH}^-$
Weak acid titrated with a strong base	Weak acid + conjugate base (buffer calculation) $\text{pH} < 7$	Salt hydrolysis calculation $\text{pH} > 7$	Use excess $[\text{OH}^-]$ to calculate pH $\text{pH} > 7$
Species in solution which affect the pH (in addition to $\text{H}_2\text{O}$ )	$\text{HA}, \text{A}^-$	$\text{A}^-$	$\text{OH}^-$
Weak base titrated with a strong acid	Weak base + conjugate acid (buffer calculation) $\text{pH} > 7$	Salt hydrolysis calculation $\text{pH} < 7$	Use excess $[\text{H}_3\text{O}^+]$ to calculate pH $\text{pH} < 7$
Species in solution which affect the pH (in addition to $\text{H}_2\text{O}$ )	$\text{B}, \text{HB}^+$	$\text{HB}^+$	$\text{H}_3\text{O}^+$

### TITRATION OF A STRONG ACID WITH A STRONG BASE

(Chemistry 8th ed. pages 713–717/9th ed. pages 727–731)

At any point during the titration of a strong acid with a strong base (or a strong base with a strong acid), the pH can be calculated from the molarity of the ion present in excess after the complete reaction. Halfway to the equivalence point the main species present are  $\text{H}_3\text{O}^+$ , the anion from the acid, and the cation from the base. The total positive charge is equal to the total negative charge; the mixture is electrically neutral.



At the equivalence point of any type of titration,  
moles  $\text{H}_3\text{O}^+ = \text{moles } \text{OH}^-$ .

For a strong acid–strong base titration, the pH equals 7.

**EXAMPLE:** Consider the titration of 40.0 mL of 0.200 M HBr by 0.100 M KOH. Calculate the pH of the resulting solution when the following volumes of KOH have been added.

a. 10.0 mL      b. 80.0 mL      c. 100.0 mL

**SOLUTION:** First, using the volume and molarity of the HBr, calculate the moles of  $\text{H}_3\text{O}^+$  to be titrated. The resulting moles of  $\text{H}_3\text{O}^+$  appear in the first column in the table at the end of the problem.

$$M = n/V$$

$$n = (0.200 \text{ mol/L})(0.0400 \text{ L}) = 8.00 \times 10^{-3} \text{ mol HBr}$$

Next, for the titration in question, calculate the moles of  $\text{OH}^-$  added from the volume and concentration of KOH. The resulting moles of  $\text{OH}^-$  used in each titration appear in the second column of the table.

$$M = n/V$$

$$n = (0.100 \text{ mol/L})(0.0100 \text{ L}) = 1.00 \times 10^{-3} \text{ mol KOH}$$

Calculate the moles of ion in excess,  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ .

	HBr +	KOH →	KBr +	HOH
Init mol	$8.00 \times 10^{-3}$	$1.00 \times 10^{-3}$	0	
Change mol	$-1.00 \times 10^{-3}$	$-1.00 \times 10^{-3}$	$+1.00 \times 10^{-3}$	
Final mol	$7.00 \times 10^{-3}$	0	$1.00 \times 10^{-3}$	

The results for each titration appear in column four in the table below.

Using the total volume, in column five of the table, and the moles of ion in excess in column four, determine the molarity of the ion in excess. The molarity of the ion in excess for each of the three titrations is in column six.

$$40.0 \text{ mL acid} + 10.0 \text{ mL base} = 50.0 \text{ mL solution}$$

$$M = n/V$$

$$M = 7.00 \times 10^{-3} \text{ mol}/0.0500 \text{ L} = 0.0140 \text{ M}$$

It is the molarity of the ion in excess which determines the pH.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.0140) = 0.854$$

In part b of the example, neither ion is in excess. The pH equals 7 because the titration is at the equivalence point.

Be careful, in part c of the example, the excess ion is the  $\text{OH}^-$  ion. To calculate the pH, you must determine pOH and then the pH.

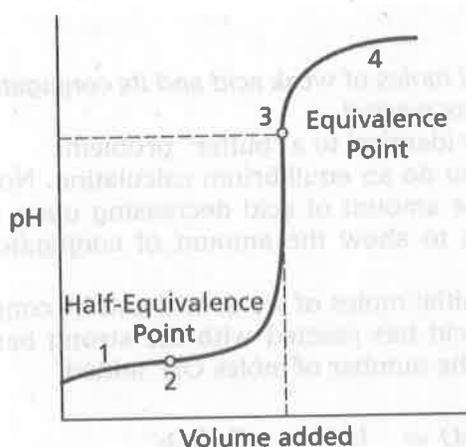
Problem Part	Mol $\text{H}_3\text{O}^+$	Mol $\text{OH}^-$	Mol Ion in Excess	Total Volume (When acid and base react)	Molarity Ion In Excess	pH
A	$8.00 \times 10^{-3}$	$1.00 \times 10^{-3}$	$7.00 \times 10^{-3}$ ( $\text{H}_3\text{O}^+$ )	0.0500 L	0.140 ( $\text{H}_3\text{O}^+$ )	0.854
B	$8.00 \times 10^{-3}$	$8.00 \times 10^{-3}$	None Equivalence point	Not needed	None	7.00
C	$8.00 \times 10^{-3}$	$10.0 \times 10^{-3}$	$2.0 \times 10^{-3}$ ( $\text{OH}^-$ )	0.140 L	0.014 ( $\text{OH}^-$ )	12.15

### AP Tip

When you are calculating the pH during a titration, be careful to take the negative log of the concentration of  $\text{H}_3\text{O}^+$ , not just the moles of  $\text{H}_3\text{O}^+$  which is a common mistake. And if the excess ion or the value of  $x$  is  $\text{OH}^-$ , be sure that you calculate the pOH and then the pH.

### TITRATION OF A WEAK ACID WITH A STRONG BASE

There are four characteristic types of calculations for the titration of a weak acid with a strong base: before the equivalence point (1), halfway to equivalence point (2), at the equivalence point (3), and after the equivalence point (4). For this type of titration, always do stoichiometric calculations followed by equilibrium calculations.



EXAMPLE: A 25.0-mL sample of 0.100 M  $\text{HC}_3\text{H}_5\text{O}_2$  is titrated with 0.100 M NaOH. Calculate the pH when the following volumes of 0.100 M NaOH are added:  $K_a = 1.3 \times 10^{-5}$  for  $\text{HC}_3\text{H}_5\text{O}_2$ .

- a) 8.0 mL      b) 12.5 mL      c) 25.0 mL      d) 30.0 mL

SOLUTION: Titration Point 1 – Calculation of the pH before the Equivalence Point

Part a of the example above involves the titration before the equivalence point. Perform the stoichiometry and record the results in a table under the reaction.

Stoichiometry:

Calculate the initial moles of the weak acid present in the sample.

$$0.0250 \text{ L} \times 0.100 \text{ mol/L} = 2.50 \times 10^{-3} \text{ mol HC}_3\text{H}_5\text{O}_2$$

Calculate the moles of strong base,  $\text{OH}^-$ , added.

$$0.0080 \text{ L} \times 0.100 \text{ mol/L} = 8.0 \times 10^{-4} \text{ mol}$$

The total volume of the solution is now 33.0 mL. Calculate the concentration of each species that remains.

$$[\text{HC}_3\text{H}_5\text{O}_2] = 1.70 \times 10^{-3} \text{ mol} / 0.0330 \text{ L} = 0.0515 \text{ M}$$

	$\text{HC}_3\text{H}_5\text{O}_2$	$\text{OH}^-$	$\text{C}_3\text{H}_5\text{O}_2^-$	$\text{H}_2\text{O}$
Init mol	$2.50 \times 10^{-3}$	$8.0 \times 10^{-4}$	0	
Change mol	$-8.0 \times 10^{-4}$	$-8.0 \times 10^{-4}$	$+8.0 \times 10^{-4}$	
Final mol	$1.70 \times 10^{-3}$	0	$8.0 \times 10^{-4}$	
Final [ ]	0.0515		0.0242	

Equilibrium:

Calculate the new initial moles of weak acid and its conjugate base present after the  $\text{OH}^-$  has reacted.

This problem is now identical to a “buffer” problem.

Make an ICE table to do an equilibrium calculation. Note the minus sign to show the amount of acid decreasing upon added  $\text{OH}^-$  and the plus sign to show the amount of conjugate base increasing.

Calculate the new initial moles of weak acid and its conjugate base, after the weak acid has reacted with the strong base, by subtracting or adding the number of moles  $\text{OH}^-$  added.

	$\text{HC}_3\text{H}_5\text{O}_2$	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	$\text{C}_3\text{H}_5\text{O}_2^-$
I	0.0515				0.0242
C	-x			+x	+x
E	$0.0515 - x$			x	$0.0242 + x$

You can now perform the equilibrium calculation.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]}$$

$$1.3 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+](0.0242 + x)}{0.0515 + x} \approx \frac{[\text{H}_3\text{O}^+]0.0242}{0.0515}$$

$$2.77 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = 4.56$$

Alternatively, you can use the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log[\text{C}_3\text{H}_5\text{O}_2^-]/[\text{HC}_3\text{H}_5\text{O}_2]$$

$$\text{pH} = -\log(1.3 \times 10^{-5}) + [\log(0.0242 + x)/(0.0515 - x)] = 4.56$$

#### Titration Point 2 – Halfway to the Equivalence Point

In part b of the example on the previous page, a 25.00-mL sample of 0.100 M  $\text{HC}_3\text{H}_5\text{O}_2$  is titrated with 12.5 of 0.100 M NaOH.  $K_a$  is  $1.3 \times 10^{-5}$  for  $\text{HC}_3\text{H}_5\text{O}_2$ .

Half of the acid being titrated is neutralized. This point is halfway to the equivalence point.

Since half the acid is neutralized and half remains,  $[\text{HA}] = [\text{A}^-]$ . The major species present at this point in the titration are  $\text{H}_3\text{O}^+$ , the anion from the acid, the cation from the base, and the weak acid. The total positive charge is equal to the total negative charge; the mixture remains electrically neutral.

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

$$[\text{HA}]$$

$$\text{p}K_a = \text{pH}$$

$$\text{p}K_a = -\log K_a = -\log (1.3 \times 10^{-5}) = 4.89$$

#### Titration Point 3 – At the Equivalence Point

In part c of the example on the previous page, a 25.00-mL sample of 0.100 M  $\text{HC}_3\text{H}_5\text{O}_2$  is titrated with 25.0 mL of 0.100 M NaOH.

$K_a$  is  $1.3 \times 10^{-5}$  for  $\text{HC}_3\text{H}_5\text{O}_2$ .

Stoichiometry:

Calculate the initial moles of the weak acid in the sample.

Calculate the moles of strong base,  $\text{OH}^-$ , added.

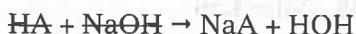
$$0.0250 \text{ L} \times 0.100 \text{ mol/L} = 2.50 \times 10^{-3} \text{ mol OH}^- = \text{mol C}_3\text{H}_5\text{O}_2^-$$

The total volume of the solution is now 50.0 mL. Calculate the concentration of each species that remains.

$$[\text{C}_3\text{H}_5\text{O}_2^-] = 2.50 \times 10^{-3} \text{ mol} / 0.0500 \text{ L} = 0.0500 \text{ M}$$

	$\text{HC}_3\text{H}_5\text{O}_2$	$\text{OH}^-$	$\text{C}_3\text{H}_5\text{O}_2^-$	$\text{H}_2\text{O}$
Init mol	$2.50 \times 10^{-3}$	$2.50 \times 10^{-3}$	0	
Change mol	$-2.50 \times 10^{-3}$	$-2.50 \times 10^{-3}$	$+2.50 \times 10^{-3}$	
Final mol	0	0	$2.50 \times 10^{-3}$	
Final [ ]			0.0500	

There is no weak acid present once the strong base added completely reacts. All that is present is  $\text{A}^-$  ( $\text{C}_3\text{H}_5\text{O}_2^-$ ), the conjugate base of weak acid, HA ( $\text{HC}_3\text{H}_5\text{O}_2$ ). An aqueous solution of  $\text{A}^-$  will be basic due to its reaction with water.



The problem from this point on is a salt hydrolysis problem.

	$\text{C}_3\text{H}_5\text{O}_2^-$	$\text{HOH}$	$\text{HC}_3\text{H}_5\text{O}_2$	$\text{OH}^-$
I	0.0500		0	0
C	-x		+x	+x
E	$0.0500 - x$		x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}$$

$$K_b = \frac{[\text{OH}^-][\text{HC}_3\text{H}_5\text{O}_2]}{[\text{C}_3\text{H}_5\text{O}_2^-]} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

$$x = [(7.7 \times 10^{-10})(0.0500)]^{1/2} = 6.2 \times 10^{-6} \text{ M OH}^-$$

$$\text{pOH} = 5.21; \text{pH} = 14.00 - 5.21 = 8.79$$

#### Titration Point 4 – After the Equivalence Point

The calculations involved here are identical to those in a strong acid–strong base titration.

In part d of the example on the previous page, a 25.0-mL sample of 0.100 M  $\text{HC}_3\text{H}_5\text{O}_2$  is titrated with 30.0 mL of 0.100 M NaOH.  $K_a$  is  $1.3 \times 10^{-5}$  for  $\text{HC}_3\text{H}_5\text{O}_2$ .

$$0.0300 \text{ L} \times 0.100 \text{ mol/L} = 3.00 \times 10^{-3} \text{ mol NaOH}$$

$$0.02500 \text{ L} \times 0.100 \text{ mol/L} = 2.50 \times 10^{-3} \text{ mol HC}_3\text{H}_5\text{O}_2$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ mol} / 0.0550 \text{ L} = 9.1 \times 10^{-3} \text{ M}$$

Stoichiometry:

	$\text{HC}_3\text{H}_5\text{O}_2 +$	$\text{OH}^- \rightarrow$	$\text{C}_3\text{H}_5\text{O}_2^- +$	$\text{H}_2\text{O}$
Init mol	$2.50 \times 10^{-3}$	$3.00 \times 10^{-3}$	0	
Change mol	$-2.50 \times 10^{-3}$	$-2.50 \times 10^{-3}$	$+2.50 \times 10^{-3}$	
Final mol	0	$5.0 \times 10^{-4}$	$2.50 \times 10^{-3}$	
Final [ ]		$9.1 \times 10^{-3}$	0.0500	

The hydrolysis of  $\text{C}_3\text{H}_5\text{O}_2^-$  will not significantly change the  $[\text{OH}^-]$ , so the pH is only dependent on the excess  $[\text{OH}^-]$ .

$$\text{pOH} = 2.0; \text{pH} = 12.0$$

### TITRATION OF A WEAK BASE WITH A STRONG ACID

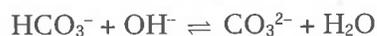
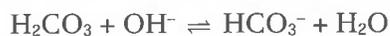
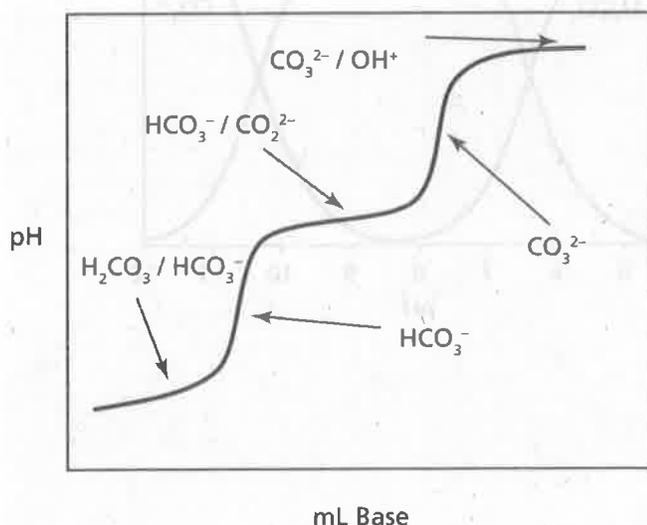
The calculations for a weak base–strong acid titration are very similar to the weak acid–strong base titration.

The differences are these:

- ❑ The pH before the equivalence point is greater than 7.
- ❑ At the equivalence point, the pH is less than 7 since the salt formed is acidic.
- ❑ After the equivalence point, the pH is determined by the molarity of the excess  $\text{H}^+$ .

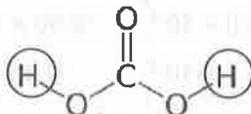
### CHARACTERISTICS OF TITRATION CURVES

It is important for you to be able to sketch and identify the key points on titration curves for the AP exam. The next example will help you to review titration curves for the different types of titrations discussed in this section. Calculations involving titrations of polyprotic acids are beyond the scope of the AP exam, but qualitative questions may be asked.

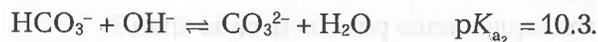
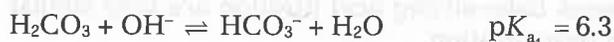


The graph above shows a titration of carbonic acid (a diprotic acid) with a strong base. Two fairly vertical regions (labeled  $\text{HCO}_3^-$  and

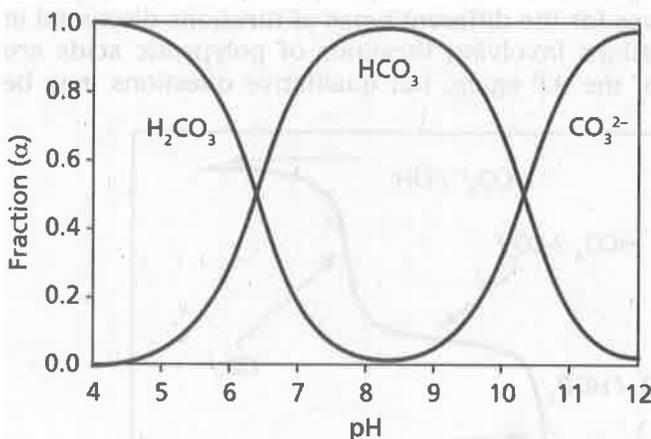
$\text{CO}_3^{2-}$ ) indicate rapid pH changes resulting from a small change in volume. This indicates 2 *labile protons*. Labile protons are protons prone to separate or be removed from the rest of the molecule; they are the “acidic” protons. The labile protons in  $\text{H}_2\text{CO}_3$  are circled in the structure below.



The species present at different points in the titration depend on the pH of the solution. Protonation is an equilibrium situation: a competition between the  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{H}_2\text{O}$ . In aqueous solution at  $25^\circ\text{C}$ ,  $\text{p}K_{a_1} = 6.3$  and  $\text{p}K_{a_2} = 10.3$ .



$\text{H}_2\text{CO}_3$  is the predominant species present at  $\text{pH} < 6.3$  because the carbonic acid has a greater affinity for protons than water does. Bicarbonate ion ( $\text{HCO}_3^-$ ) is predominant at  $6.3 < \text{pH} < 10.3$  and carbonate ion ( $\text{CO}_3^{2-}$ ) predominates at  $\text{pH} > 10.3$ . The speciation graph below shows how the fraction of  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  depend on the pH of the solution.



EXAMPLE: The questions that follow refer to the following three titration curves. All solutions are equimolar.

Figure 1:

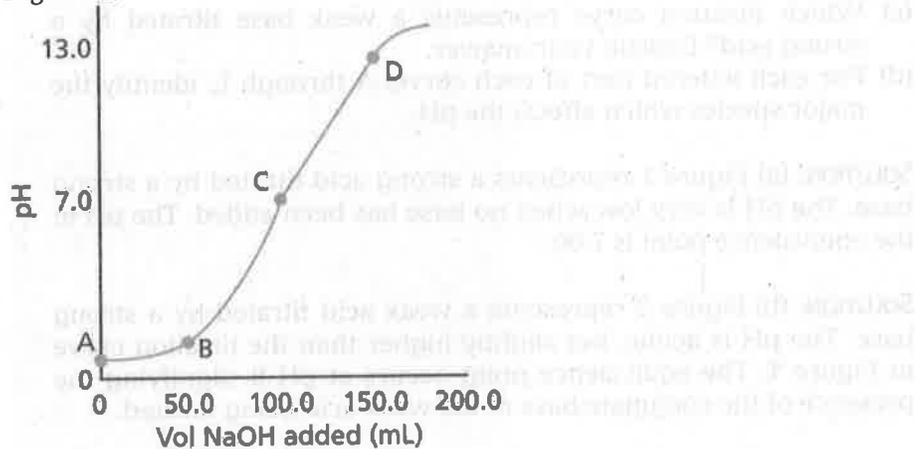


Figure 2:

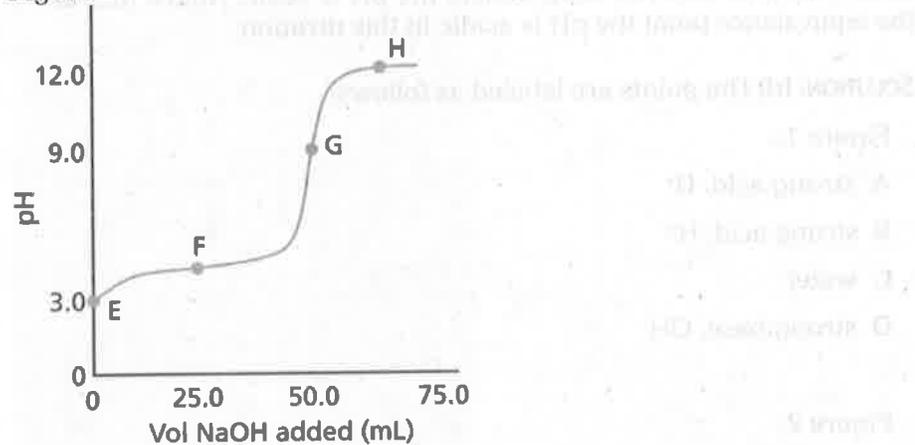
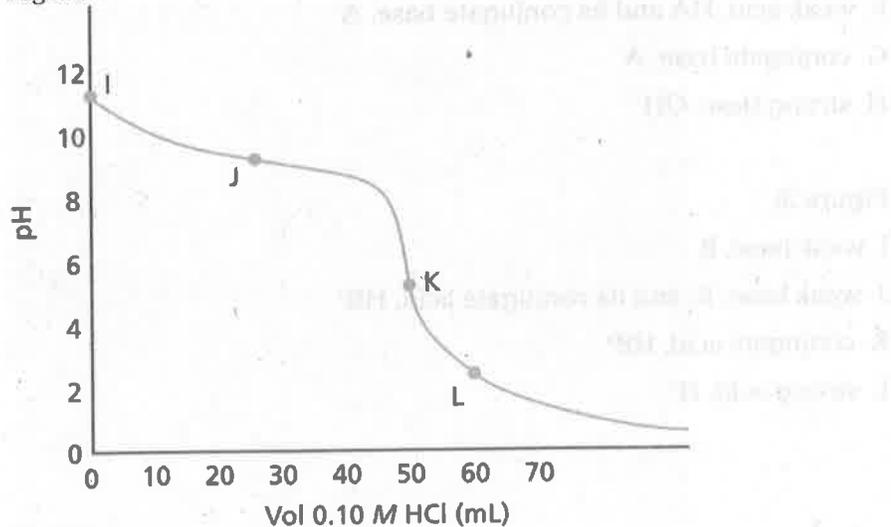


Figure 3:



- (a) Which titration curve represents a strong acid titrated by a strong base? Explain your answer.
- (b) Which titration curve represents a weak acid titrated by a strong base? Explain your answer.
- (c) Which titration curve represents a weak base titrated by a strong acid? Explain your answer.
- (d) For each lettered part of each curve, A through L, identify the major species which affects the pH.

**SOLUTION:** (a) Figure 1 represents a strong acid titrated by a strong base. The pH is very low when no base has been added. The pH at the equivalence point is 7.00.

**SOLUTION:** (b) Figure 2 represents a weak acid titrated by a strong base. The pH is acidic, but slightly higher than the titration curve in Figure 1. The equivalence point occurs at pH 9, signifying the presence of the conjugate base of the weak acid being titrated.

**SOLUTION:** (c) Figure 3 represents a weak base titrated by a strong acid. When no acid has been added, the pH is basic. Notice that at the equivalence point the pH is acidic in this titration.

**SOLUTION:** (d) The points are labeled as follows:

Figure 1:

- A strong acid,  $H^+$
- B strong acid,  $H^+$
- C water
- D strong base,  $OH^-$

Figure 2:

- E weak acid, HA
- F weak acid, HA and its conjugate base,  $A^-$
- G conjugate base,  $A^-$
- H strong base,  $OH^-$

Figure 3:

- I weak base, B
- J weak base, B, and its conjugate acid,  $HB^+$
- K conjugate acid,  $HB^+$
- L strong acid,  $H^+$

## THERMODYNAMICS OF SOLUTION FORMATION

(Chemistry 8th ed. pages 501–504/9th ed. pages 514–517)

The common axiom, “like dissolves like” is an inadequate explanation for any AP Chemistry exam question that asks you to explain why 2 substances may be soluble or insoluble. In order to understand why that axiom is used, you need to understand solution formation in terms of thermodynamics: enthalpy, entropy, and free energy.

The attractive forces that hold the solute and solvent together must first be overcome before a solution can form. Since both of these processes involve overcoming intermolecular attractions, expanding the solute ( $\Delta H_1$ ) and expanding the solvent ( $\Delta H_2$ ) are always endothermic. Attraction between the solute and solvent ( $\Delta H_3$ ) is usually (but not always) an exothermic process. The enthalpy of solution ( $\Delta H_{\text{soln}}$ ) is the sum of the  $\Delta H$  for the entire process.

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

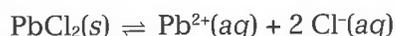
If  $\Delta H_{\text{soln}}$  is positive (as is for the case of dissolving NaCl:  $\Delta H_{\text{soln}} = 3$  kJ/mol), then entropy must be the driving force that makes  $\Delta G^\circ$  negative and explains why salt spontaneously dissolves in water.

## SOLUBILITY PRODUCT

(Chemistry 8th ed. pages 744–745, 748/9th ed. pages 759–760, 763)

You must memorize the fact that all sodium, potassium, ammonium, and nitrate salts are soluble in water. For all other salts, you will either be given solubility information or will need to calculate solubility based on equilibrium data and/or constants provided to you.

For slightly soluble or insoluble salts, equilibrium exists between the solid and its aqueous ions. For example, lead(II) chloride dissolves in water as follows:



At first, when the salt is added to the water, there are no ions present. As the solid dissolves, the concentration of the ions increases. A simultaneous competing process is the reverse of the dissolution, that is, the reforming of the solid called crystallization. At some point, the maximum amount of dissolution is achieved, which is called the saturation point. However, remember that on a molecular level, a dynamic equilibrium exists between dissolved solute and undissolved solid. (The rate of dissolution equals the rate of crystallization.) The solution is saturated when no more solid dissolves and equilibrium is reached.

The equilibrium expression for the dissolution of lead(II) chloride is

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

The constant,  $K_{\text{sp}}$ , is the solubility product constant. For salts producing the same number of ions, the  $K_{\text{sp}}$  value can be used to measure the extent to which the solid dissolves. The larger the  $K_{\text{sp}}$  value, the more soluble the salt.

**EXAMPLE:** Given the following salts and their  $K_{sp}$  values, which salt is the most soluble? Which salt is the least soluble?

Formula	$K_{sp}$
$\text{NiCO}_3$	$1.4 \times 10^{-7}$
$\text{MnS}$	$2.3 \times 10^{-13}$
$\text{CaSO}_4$	$6.1 \times 10^{-5}$

**SOLUTION:** The most soluble salt is the salt with the largest  $K_{sp}$  value,  $\text{CaSO}_4$ .

The least soluble salt is the salt with the lowest value of  $K_{sp}$ ,  $\text{MnS}$ . You are able to compare the  $K_{sp}$  values to determine the relative solubilities of the salts because they all produce the same number of ions.

## CALCULATIONS INVOLVING SOLUBILITY

(Chemistry 8th ed. pages 743–749/9th ed. pages 758–765)

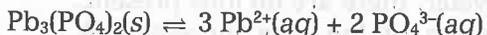
The solubility of a salt is the amount of salt that will dissolve in 1 liter of water. The solubility of a salt can be given in units of mol/L or g/L. The solubility of a salt can be used to determine the  $K_{sp}$  value for the salt.

### CALCULATING $K_{sp}$ FROM SOLUBILITY

**EXAMPLE:** The solubility of  $\text{Pb}_3(\text{PO}_4)_2$  is  $6.2 \times 10^{-12}$  M. Calculate the  $K_{sp}$  value for the solid.

$K_{sp}$  equals  $9.9 \times 10^{-55}$ .

Step 1: Write the reaction for the dissolution of the solid.



Step 2: Underneath the reaction, make an ICE chart.

	$\text{Pb}_3(\text{PO}_4)_2(\text{s})$	$\rightleftharpoons$	$3 \text{Pb}^{2+}(\text{aq})$	+	$2 \text{PO}_4^{3-}(\text{aq})$
I			0		0
C			+3x		+2x
E			3x		2x

In the ICE chart above,  $x$  represents  $x$  mol/L of  $\text{Pb}_3(\text{PO}_4)_2(\text{s})$  dissolving to reach equilibrium which equals  $6.2 \times 10^{-12}$  M. Remember that pure solids are not included in equilibrium expressions.

For every 1 mol per liter of  $\text{Pb}_3(\text{PO}_4)_2$  which dissolves, 3 moles per liter of  $\text{Pb}^{2+}$  and 2 moles per liter of  $\text{PO}_4^{3-}$  form.

$3x$  is the mol/L of  $\text{Pb}^{2+}(\text{aq})$  produced when the solid,  $\text{Pb}_3(\text{PO}_4)_2$ , dissolves.

$2x$  is the mol/L of  $\text{PO}_4^{3-}(\text{aq})$  produced when the solid,  $\text{Pb}_3(\text{PO}_4)_2$ , dissolves.

Step 3: Write the equilibrium expression for the reaction and plug in the values from the equilibrium line of the ICE chart.

$$K_{\text{sp}} = [\text{Pb}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3x)^3(2x)^2 = 108x^5$$

The value of  $x$  is the solubility of  $\text{Pb}_3(\text{PO}_4)_2$ , which equals  $6.2 \times 10^{-12} \text{ M}$ .

$$K_{\text{sp}} = 108(6.2 \times 10^{-12})^5 = 9.9 \times 10^{-55}$$

Alternate solution:

$$6.2 \times 10^{-12} \frac{\text{mol Pb}_3(\text{PO}_4)_2}{1 \text{ L}} \times \frac{3 \text{ mol Pb}^{2+}}{1 \text{ mol Pb}_3(\text{PO}_4)_2} = 1.9 \times 10^{-11} \text{ M Pb}^{2+}$$

$$6.2 \times 10^{-12} \frac{\text{mol Pb}_3(\text{PO}_4)_2}{1 \text{ L}} \times \frac{2 \text{ mol PO}_4^{3-}}{1 \text{ mol Pb}_3(\text{PO}_4)_2} = 1.2 \times 10^{-11} \text{ M PO}_4^{3-}$$

Plug these values into the  $K_{\text{sp}}$  expression and solve for  $K_{\text{sp}}$ .

$$K_{\text{sp}} = [\text{Pb}^{2+}]^3[\text{PO}_4^{3-}]^2 = (1.9 \times 10^{-11})^3(1.2 \times 10^{-11})^2 = 9.9 \times 10^{-55}$$

### CALCULATING SOLUBILITY FROM $K_{\text{sp}}$

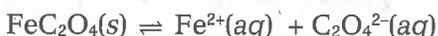
If you are given a group of salts which do not all have the same cation to anion ratio and asked which is more soluble, you must perform a calculation to determine the solubility of each salt.

**EXAMPLE:** Given the two salts in the table below, which is more soluble? Show calculations to support your answer.

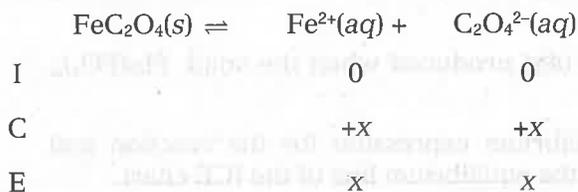
	$K_{\text{sp}}$
$\text{FeC}_2\text{O}_4$	$2.1 \times 10^{-7}$
$\text{Cu}(\text{IO}_4)_2$	$1.4 \times 10^{-7}$

**SOLUTION:** You cannot directly compare the  $K_{\text{sp}}$  values to predict which is more soluble because the salts dissolve to produce a different number of ions.  $\text{FeC}_2\text{O}_4$  dissolves to produce two ions and  $\text{Cu}(\text{IO}_4)_2$  produces three ions. You must calculate the solubility for each salt from its  $K_{\text{sp}}$  value.

Step 1: Write the reaction for the dissolution of the solid.



Step 2: Underneath the reaction, make an ICE chart.



Step 3: Write the equilibrium expression for  $K_{\text{sp}}$ , plug in the equilibrium line, and solve for  $x$ .

$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

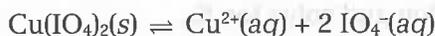
$$2.1 \times 10^{-7} = x^2$$

$$x = 4.6 \times 10^{-4} \text{ mol Fe}^{2+}/\text{L}$$

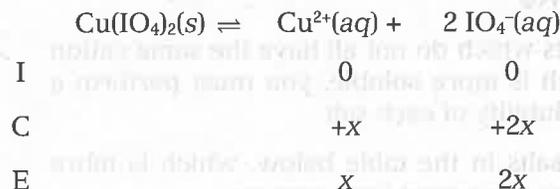
$$4.6 \times 10^{-4} \text{ mol Fe}^{2+} \times \frac{1 \text{ mol FeC}_2\text{O}_4}{1 \text{ L}} = 4.6 \times 10^{-4} \text{ mol FeC}_2\text{O}_4/\text{L}$$

Repeat the same calculations for the next salt.

Step 1: Write the reaction for the dissolution of the solid.



Step 2: Underneath the reaction, make an ICE chart.



Step 3: Write the equilibrium expression for  $K_{\text{sp}}$ , plug in the equilibrium line, and solve for  $x$ .

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{IO}_4^{-}]^2$$

$$1.4 \times 10^{-7} = x(2x)^2$$

$$1.4 \times 10^{-7} = 4x^3$$

$$x = 3.3 \times 10^{-3} \text{ mol/L}$$

$$3.3 \times 10^{-3} \text{ mol Cu}^{2+} \times \frac{1 \text{ mol Cu}(\text{IO}_4)_2}{1 \text{ L}} = \frac{3.3 \times 10^{-3} \text{ mol Cu}(\text{IO}_4)_2}{\text{L}}$$

$$3.3 \times 10^{-3} \text{ mol Cu}(\text{IO}_4)_2/\text{L} \text{ is greater than } 4.6 \times 10^{-4} \text{ mol FeC}_2\text{O}_4/\text{L}.$$

Therefore  $\text{Cu}(\text{IO}_4)_2$  is more soluble even though  $K_{\text{sp}}$  for  $\text{FeC}_2\text{O}_4$  is slightly larger than  $K_{\text{sp}}$  for  $\text{Cu}(\text{IO}_4)_2$ .

## COMMON ION EFFECT

(Chemistry 8th ed. pages 750–752/9th ed. pages 765–767)

When a salt is dissolved in water containing a common ion, its solubility is decreased.

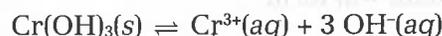
For example, consider the solubility equilibrium of silver sulfate.



When silver sulfate is dissolved in 0.100 M AgNO<sub>3</sub>, the Ag<sup>+</sup> ion from silver nitrate causes the equilibrium to shift to the left, decreasing the solubility of silver sulfate.

## pH AND SOLUBILITY

Chromium(III) hydroxide dissolves according to the equilibrium



An increase in pH, caused by the addition of OH<sup>-</sup> ions, will shift the equilibrium to the left, decreasing the solubility of Cr(OH)<sub>3</sub>.

A decrease in pH, caused by the addition of H<sup>+</sup> ions, will shift the equilibrium to the right, increasing the solubility of Cr(OH)<sub>3</sub>. The H<sup>+</sup> ions remove the OH<sup>-</sup> ions from the solution.

A salt with the general formula, MX, will show increased solubility in acidic solution if the anion, X<sup>-</sup>, is an effective base (if HX is a weak acid). Common anions that make effective bases include S<sup>2-</sup>, OH<sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>.

## PRECIPITATE FORMATION

(Chemistry 8th ed. pages 752–755/9th ed. pages 768–771)

A precipitate may or may not form when two solutions are mixed, depending on the concentrations of the ions involved in the formation of the solid.

## ION PRODUCT

The ion product, *Q*, is written in the same way as the *K*<sub>sp</sub> expression.

For lead(II) chloride,  $Q = [\text{Pb}^{2+}][\text{Cl}^-]^2$

Calculation of the value, *Q*, involves the use of the initial concentrations of the solutions mixed, [Pb<sup>2+</sup>]<sub>0</sub> and [Cl<sup>-</sup>]<sub>0</sub>, instead of the equilibrium concentrations.

A comparison of the value of *Q* to *K*<sub>sp</sub> determines if a precipitate is formed.

$Q > K_{sp}$ : precipitation occurs

$Q < K_{sp}$ : no precipitation occurs

$Q = K_{sp}$ : the solution is saturated

**EXAMPLE:** Will a precipitate form when 100.0 mL of 4.0 × 10<sup>-4</sup> M Mg(NO<sub>3</sub>)<sub>2</sub> is added to 100.0 mL of 2.0 × 10<sup>-4</sup> M NaOH?

**SOLUTION:** Step 1: Determine the identity of the precipitate formed.

$\text{Mg}(\text{OH})_2$  is the precipitate.  $\text{NaNO}_3$  is always soluble.

Step 2: Determine the concentration of the ions after they are mixed and before any reaction occurs.

Determine the moles of concentration of each solute present. Be sure to divide by the total volume of the two solutions mixed.

$$[\text{Mg}^{2+}]_0 = (0.1000 \text{ L} \times 4.0 \times 10^{-4} \text{ mol/L}) / 0.2000 \text{ L} = 2.0 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-]_0 = (0.1000 \text{ L} \times 2.0 \times 10^{-4} \text{ mol/L}) / 0.2000 \text{ L} = 1.0 \times 10^{-4} \text{ M}$$

Step 3: Write the ion product expression, calculate its value, and compare it to  $K_{sp}$ , which equals  $8.8 \times 10^{-12}$ .

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$Q = (2.0 \times 10^{-4})(1.0 \times 10^{-4})^2 = 2.0 \times 10^{-12}$$

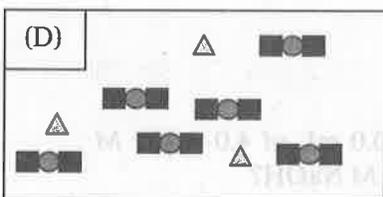
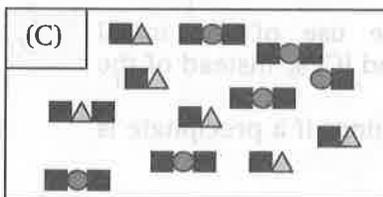
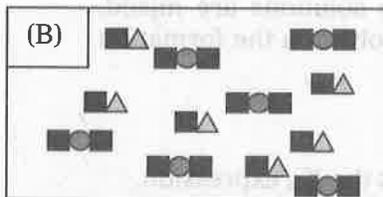
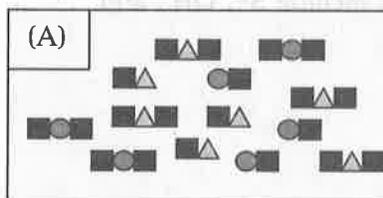
Since  $Q < K_{sp}$ , no precipitate will form.

## MULTIPLE-CHOICE QUESTIONS

No calculators are to be used in this section.

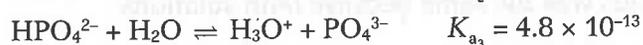
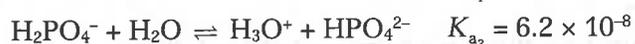
1. Equal volumes of equimolar  $\text{H}_2\text{S}$  and  $\text{OH}^-$  are combined. Which diagram represents the resultant solution?

S =  $\blacktriangle$       O =  $\bullet$       H =  $\blacksquare$



2. The autoionization of water is an endothermic process. How would pH of pure water change if the water was at 100°C?
- (A) pH would remain 7 because water is neutral.  
 (B) pH would decrease because equilibrium shifts towards  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ .  
 (C) pH would increase because equilibrium shifts towards  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ .  
 (D) pH could not be measured because water boils at 100°C.

3. Consider the phosphoric acid equilibria.



What species is predominant at pH 12?

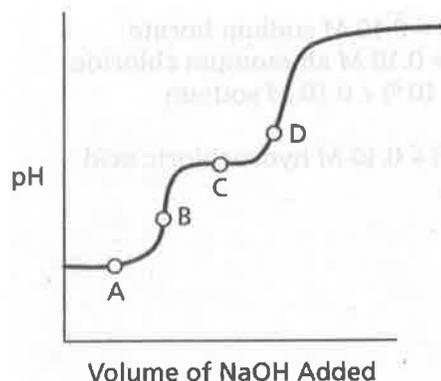
- (A)  $\text{H}_3\text{PO}_4$   
 (B)  $\text{H}_2\text{PO}_4^-$   
 (C)  $\text{HPO}_4^{2-}$   
 (D)  $\text{PO}_4^{3-}$
4. Each of the following salts has a solubility of  $1.0 \times 10^{-5} \text{ M}$ . Rank the salts in order of lowest to highest  $K_{\text{sp}}$ .  
 AX,  $\text{B}_2\text{X}$ ,  $\text{C}_2\text{X}_3$ ,  $\text{D}_3\text{X}$
- (A)  $\text{C}_2\text{X}_3 < \text{D}_3\text{X} < \text{B}_2\text{X} < \text{AX}$   
 (B)  $\text{C}_2\text{X}_3 < \text{D}_3\text{X} < \text{AX} < \text{B}_2\text{X}$   
 (C)  $\text{D}_3\text{X} < \text{C}_2\text{X}_3 < \text{B}_2\text{X} < \text{AX}$   
 (D)  $\text{D}_3\text{X} < \text{B}_2\text{X} < \text{AX} < \text{C}_2\text{X}_3$
5. 0.10 mol  $\text{NaC}_2\text{H}_3\text{O}_2$  and 0.050 mol HCl was added to 1.0 L of 0.075 M  $\text{HC}_2\text{H}_3\text{O}_2$ . List the species in order of decreasing equilibrium concentration.
- (A)  $[\text{HC}_2\text{H}_3\text{O}_2] > [\text{C}_2\text{H}_3\text{O}_2^-] > [\text{Cl}^-] > [\text{H}_3\text{O}^+]$   
 (B)  $[\text{H}_3\text{O}^+] > [\text{Cl}^-] > [\text{C}_2\text{H}_3\text{O}_2^-] > [\text{HC}_2\text{H}_3\text{O}_2]$   
 (C)  $[\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-] > [\text{Cl}^-] = [\text{H}_3\text{O}^+]$   
 (D)  $[\text{Cl}^-] = [\text{H}_3\text{O}^+] > [\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-]$

6. Two unlabeled Erlenmeyer flasks each contained 25.00 mL of solution at pH 4.00. Each flask was titrated with the same standardized NaOH solution. The volumes needed to reach the endpoint are listed in the table below. What claim can be made about the acids in flasks A and B?

Flask	Titrant Volume (mL)
A	11.29
B	37.07

- (A) The concentration of the acids was the same because both solutions were pH 4.00.
- (B) The strength of the acids was the same because both solutions were pH 4.00.
- (C) Flask A was a strong acid because less titrant was needed to reach the endpoint.
- (D) Flask B was a strong acid because more titrant was needed to reach the endpoint.
7. Consider the following data for the dissolution of an alcohol, R-OH, in a solvent, X-OH.  $\Delta H_1 = 65 \text{ kJ/mol}$ ,  $\Delta H_2 = 340 \text{ kJ/mol}$ ,  $\Delta H_3 = -8 \text{ kJ/mol}$ . Predict and explain the solubility of this compound.
- (A) The compound would be soluble because the solute and solvent both have -OH in their formulas.
- (B) The compound would not be soluble because  $\Delta H_3$  is negative and exothermic.
- (C) The compound would not be soluble because  $\Delta H_{\text{soln}} = 397 \text{ kJ/mol}$  which is very endothermic.
- (D) The compound would not be soluble because  $\Delta S$  is unknown.
8. HA is a weak acid which is 4.0% dissociated at 0.100 M. Determine the  $K_a$  for this acid.
- (A) 0.0040
- (B) 0.00016
- (C) 0.040
- (D) 1.6

9. What point on the graph represents  $pK_{a_2}$ ?



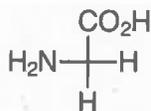
- (A) A  
(B) B  
(C) C  
(D) D
10. A buffer can maintain pH upon addition of small amounts of a strong base because
- (A) small amounts of base do not drastically alter an aqueous solution's pH  
(B) the strong base is balanced by the weak acid and conjugate base in the buffer  
(C) the weak acid reacts with the strong base to make more conjugate base  
(D) the strong base has a different pH than the buffer
11. Which acid is the strongest acid?

Acid	$K_a$
HF	$7.2 \times 10^{-4}$
HNO <sub>2</sub>	$4.0 \times 10^{-4}$
HCO <sub>2</sub> H	$1.8 \times 10^{-4}$
HC <sub>3</sub> H <sub>5</sub> O <sub>3</sub>	$1.38 \times 10^{-4}$

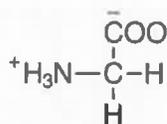
- (A) HF  
(B) HNO<sub>2</sub>  
(C) HCO<sub>2</sub>H  
(D) HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>
12. Which of the following describes what happens to the solubility of a slightly soluble ionic compound when a common ion is added to the solution?
- (A) The solubility of the ionic compound is reduced.  
(B) The solubility of the ionic compound is increased.  
(C) There is no effect on the solubility of the ionic compound.  
(D) The ionic compound dissolves more rapidly.

13. A researcher needs to prepare a pH 5 buffer. What solutions would be best?
- (A) 0.20 M boric acid ( $K_a = 5.8 \times 10^{-10}$ ) + 0.10 M sodium borate  
 (B) 0.20 M ammonia ( $K_b = 1.8 \times 10^{-5}$ ) + 0.10 M ammonium chloride  
 (C) 0.20 M propanoic acid ( $K_a = 1.3 \times 10^{-5}$ ) + 0.10 M sodium hydroxide  
 (D) 0.20 M lactic acid ( $K_a = 1.38 \times 10^{-4}$ ) + 0.10 M hydrochloric acid

I.



II.



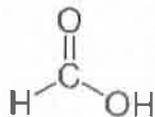
$\text{p}K_a$  carboxylic acid = 2.34

$\text{p}K_a$  protonated amine = 9.6

14. The structures of the amino acid, glycine, are shown above. What is the predominant form of the amino acid at physiological pH 7.3?
- (A) only structure I  
 (B) fairly equal amounts of structures I and II  
 (C) more structure II than structure I  
 (D) only structure II
15. Two salts, AX and  $\text{BX}_2$ , have identical  $K_{sp}$  values at a given temperature. We can say
- (A) the salts are more soluble in 0.1 M NaX than in water  
 (B) the molar solubility of AX is identical to  $\text{BX}_2$   
 (C) addition of NaX will not affect the solubilities of the salts  
 (D) the molar solubility of AX is greater than that of  $\text{BX}_2$

### FREE-RESPONSE QUESTIONS

1. Methanoic (formic) acid is responsible for the pain of bee stings and stinging nettles.  $K_a = 1.8 \times 10^{-4}$
- (a) Circle the labile proton in the structure.



- (b) 15.00 mL of formic acid was titrated with 29.07 mL of 0.0896 M potassium hydroxide.
- (i) Write the net ionic equation for the reaction.  
 (ii) Calculate the concentration of formic acid solution.  
 (iii) Is the pH at the equivalence point <7, 7, or >7? Explain your answer.
- (c) A different solution of formic acid had a pH of 1.62. Calculate the concentration of formic acid in that solution.

- (d) Calculate the pH of a mixture of 1.5 M formic acid and 0.500 M sodium formate.
2. Human bodies maintain their balance (homeostasis) through a series of equilibria. One important equilibrium involves calcium ion because  $\text{Ca}^{2+}$  is important for muscle contractions in the heart as well as for strong bones. Bone is a complex tissue consisting of living cells and non-living material. Calcium phosphate is part of the non-living material and is how the body stores calcium.
- (a) Write the solubility product expression for the dissolution of calcium phosphate.
- (b) When blood calcium ion concentration decreases, a hormone is released that causes calcium ions from the bones to be released into the bloodstream. What effect does this have on the concentration of calcium phosphate in the bones?



- (c) Blood pH is approximately 7.4 in healthy people. What are the predominant forms of phosphate in the blood at this pH? Justify your answer.
- (d) One way skeletons can be cleaned for study is to boil the bones in a solution to remove all material and leave the bone. Based on the equilibrium equations above, would a highly acidic or highly basic solution be best to clean the bones? Explain your answer.

## Answers

### MULTIPLE-CHOICE QUESTIONS

- B** Equal volumes of equimolar solutions have the same number of moles. The products of the reaction are equal moles of  $\text{HS}^-$  and  $\text{H}_2\text{O}$  (*Chemistry* 8th ed. pages 103–107/9th ed. pages 108–114). LO 6.11
- B** Endothermic reactions shift to products to relieve stress. Higher  $[\text{H}_3\text{O}^+]$  means lower pH (*Chemistry* 8th ed. pages 624–626/9th ed. pages 637–639). LO 6.14
- D** At high pH,  $\text{OH}^-$  is the predominant  $\text{H}^+$  acceptor so  $\text{PO}_4^{3-}$  is the predominant form of phosphate (*Chemistry* 8th ed. pages 639–642/9th ed. pages 653–656). LO 6.19

4. A  $C_2X_3$  forms the most ions so it will have the lowest calculated  $K_{sp}$ .  
AX forms the fewest ions so it will have the highest  $K_{sp}$ .

Compound	$K_{sp}$
AX	$1.0 \times 10^{-10}$
$B_2X$	$4.0 \times 10^{-15}$
$C_2X_3$	$1.1 \times 10^{-23}$
$D_3X$	$2.7 \times 10^{-19}$

(Chemistry 8th ed. pages 749–750/9th ed. pages 764–765). LO 6.22

5. A Do a stoichiometry table and then an equilibrium table.

	$NaC_2H_3O_2$	+	HCl	→	$HC_2H_3O_2$	+	NaCl
init mol	0.10		0.050		0.075		0
change in mol	-0.050		-0.050		+0.050		+0.050
final mol	0.05		0		0.125		0.050

	$HC_2H_3O_2$	+	$H_2O$	⇌	$C_2H_3O_2^-$	+	$H_3O^+$
I	0.125				0.05		0
C	-x				+x		+x
E	$0.125 + x$				$0.05 + x$		x

$$[HC_2H_3O_2] \approx 0.125 \text{ M}$$

$$[C_2H_3O_2^-] = (0.05 + x) \text{ M}$$

$$[Cl^-] = 0.050 \text{ M}$$

$$[H_3O^+] = x \text{ M}$$

(Chemistry 8th ed. page 701–704/9th ed. pages 715–718). LO 6.17

6. C At the same pH, a strong acid has a lower concentration because all of the acid is dissociated. In order for the weak acid to ionize to have the same  $[H_3O^+]$ , the concentration of HA must be much higher (Chemistry 8th ed. pages 650–657/9th ed. pages 665–671). LO 6.12

7. C A very endothermic process could not be mitigated by an increase in entropy so the dissolution is not favorable at this particular temperature (Chemistry 8th ed. pages 501–504/9th ed. pages 514–517). LO 6.24

8. B

$$[HA]_0 = 0.100 \text{ M}$$

$$[H^+] = [A^-] = 0.004 \text{ M}$$

$$K_a = [H^+][A^-]/[HA] = (0.004)(0.004)/0.100 =$$

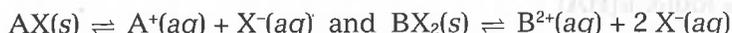
(seen more simply for our purposes here)

$$(4 \times 10^{-3})(4 \times 10^{-3})/(10^{-1}) = 1.6 \times 10^{-4}$$

Note that although the actual value for  $[HA]$  is  $0.100 - 0.004 = 0.096 \text{ M}$ , this approximation is within the 5% rule, and students do not

have calculators for this part of the test (*Chemistry* 8th ed. pages 657–659/9th ed. pages 672–673). LO 6.12

9. C Halfway to the second equivalence point (*Chemistry* 8th ed. pages 719–720/9th ed. pages 732–734). LO 6.13
10. C Buffers have WA-CB equilibrium so small additions of base will just react with the WA forming CB. CB will react with water to reform WA until equilibrium is reestablished (*Chemistry* 8th ed. pages 704–706/9th ed. pages 718–720). LO 6.20
11. A HF has the largest  $K_a$  which means its equilibrium lies farthest to products (*Chemistry* 8th ed. pages 642–643/9th ed. pages 656–657). LO 6.11
12. A The solubility of a slightly soluble ionic compound is always lowered whenever the solution already contains ions common in the solid or ions common to the solid that are added after a solution is prepared. The common-ion effect is an example of Le Châtelier's principle (*Chemistry* 8th ed. pages 750–752/9th ed. pages 766–768). LO 6.23
13. C The NaOH (limiting reagent) will react with half of the propanoic acid leaving equal concentrations of propanoic acid and propanoate ion (*Chemistry* 8th ed. pages 701–710/9th ed. pages 715–724). LO 6.18
14. C Equilibrium lies closer to structure II at pH 7.3. However, since structure does not fully deprotonate until pH 9.6 there will still be some structure I. LO 6.19
15. D For each salt, the respective solubility equilibrium expressions are:



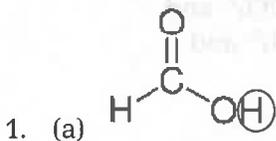
Since they have the same  $K_{sp}$  values, let us call that value  $N$ .

Let "a" represent the solubility of AX. Thus,  $(a)(a) = N$  or  $a = \sqrt{N}$ .

Let "b" represent the solubility of  $BX_2$ . Thus  $(b)(2b)^2 = N$  or  $b = \sqrt[3]{N/4}$ .

Since  $a > b$  the molar solubility of AX is greater than that of  $BX_2$  (*Chemistry* 8th ed. pages 748–750/9th ed. pages 763–766). LO 6.21

### FREE-RESPONSE QUESTIONS



The labile proton is the one that will be ionized. Because oxygen is more electronegative, it pulls electrons away from

hydrogen allowing hydrogen to become more attracted to water (*Chemistry* 8th ed. pages 677–678/9th ed. pages 691–693).  
LO 6.19



(ii) For a 1:1 stoichiometric titration,  $M_A V_A = M_B V_B$

$$M_A(15.00 \text{ mL}) = (0.0896 \text{ M})(29.07 \text{ mL})$$

$$M_A = 0.174 \text{ M}$$

(iii) The pH will be  $>7$  because a WA-SB titration makes the conjugate base of a WA as a product. The CB competes for  $\text{H}^+$  from water leaving  $\text{OH}^-$  in solution (*Chemistry* 8th ed. pages 717–722/9th ed. pages 731–736). LO 6.13

(c)  $[\text{H}_3\text{O}^+] = 10^{-1.62} = 0.024 \text{ M} = [\text{HCOO}^-]$

	$\text{HCOOH} +$	$\text{H}_2\text{O} \rightleftharpoons$	$\text{HCOO}^- +$	$\text{H}_3\text{O}^+$
I	$x$		$0$	$0$
C	$-0.024$		$+0.024$	$+0.024$
E	$x - 0.024$		$0.024$	$0.024$

$$K_a = [\text{H}_3\text{O}^+][\text{HCOO}^-]/[\text{HCOOH}]$$

$$[\text{HCOOH}] = (x - 0.024) = (0.024)^2/1.8 \times 10^{-4}$$

$$[\text{HCOOH}] = 3.2 \text{ M}$$

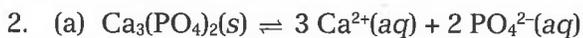
(d) You can use the Henderson–Hasselbalch equation because the equilibrium concentrations of HA and  $\text{A}^-$  are more than 1000 times greater than  $K_a$ .

$$\text{H} = \text{p}K_a + \log[\text{A}^-]/[\text{HA}]$$

$$= 3.74 + \log(0.500/1.5)$$

$$= 3.27$$

(*Chemistry* 8th ed. pages 701–710/9th ed. pages 715–724). LO 6.15



$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

(b) The concentration of calcium phosphate does not change since it is a pure solid. The moles per volume remains constant.

(c) At pH 7.4 the predominant forms of phosphate are  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ .  $\text{p}K_{a_2}$  is 7.21 which is the pH at which the  $\text{HPO}_4^{2-}$  and

$\text{H}_2\text{PO}_4^-$  would be in equal concentration. Since the physiological pH is slightly higher than this,  $\text{HPO}_4^{2-}$  has a slightly higher concentration because the labile proton is more attracted to water.

- (d) A highly basic solution will prevent the bones from being damaged in the cleaning. At high pH, acid–base equilibrium favors  $\text{PO}_4^{3-}$ . Higher  $\text{PO}_4^{3-}$  concentrations shift the solubility equilibrium back to solid  $\text{Ca}_3(\text{PO}_4)_2$  (*Chemistry* 8th ed. pages 744–752/9th ed. pages 759–768). LO 6.23

