CHEM 1332 (A.M. Guloy)

CHEMICAL EQUILIBRIA--ACID/BASE

Acid/base problems may fall into 4 categories: ***strong acid/base, weak acid/base, buffers and hydrolysis***. We will go through examples of each of these types of problems one at a time.

Strong Acids and Strong Bases

The strength of the acid is determined by how far the equilibrium lies to the right. Qualitatively, this may be judged by the $\mathbf{K_a}$ of the acid. *A large K_a indicates a strong acid; a small K_a indicates a weak acid*.

Strong acids, such as HCl, have K_a values in the vicinity of infinity. This implies that the dissociation of HCl is virtually complete, and the equilibrium lies completely to the right, therefore, the concentration of the acid equals the concentration of hydronium ions produced.

For instance, a 0.01 M HCl solution will completely dissociate into 0.01 M H_3O^+ and 0.01 M Cl^-. The effective concentration of HCl after "equilibrium" has been reached will be zero!

Analogously, strong bases, such as NaOH, will dissociate completely. The concentration of OH^- in solution will be equal to the concentration of the strong base.

A typical strong acid problem might be: What is the pH of a 0.010 M HCl solution?

Since HCl is a strong acid, the hydronium ion concentration will be equal to the HCl concentration:

$$[H_3O^+] = 0.010\ M$$

The pH can be found by taking the negative log of the hydronium ion concentration:

$$pH = -\log[H_3O^+] = -\log(0.010) = 2.00$$

A typical strong base problem might be: What is the pH of a 0.010 M NaOH solution? Since NaOH is a strong base, the hydroxide ion concentration will be equal to the NaOH concentration:

$$[OH^-] = 0.010\ M$$

The pH can be found by first finding the pOH by taking the negative log of the hydroxide ion concentration, and then converting the pH to pOH. To find the pOH:

$$pOH = -\log[OH^-] = -\log(0.010) = 2.00$$

The pH can then be calculated from the equation pH + pOH = 14:

$$pH = 14.00 - 2.00 = 12.00$$

Weak Acids and Bases

Weak acids and weak bases do not dissociate completely. An equilibrium exists between the weak acid, water, H_3O^+, and the anion of the weak acid. The equilibrium lies to the left hand side of the equation, indicating that not much H_3O^+ is being produced. The fact that very little H_3O^+ is being produced is the definition of a weak acid. The K_a for a weak acid is small, usually a number less than 1.
There are three types of problems encountered with weak acids or bases: dissociation, buffers or hydrolysis. We'll look at each type in detail.

Dissociation of a Weak Acid

In this type of problem, you will be asked to find the hydronium ion concentration and/or the pH of a weak acid whose initial concentration is known. A typical problem may be:

What is the hydronium ion concentration and pH of a 0.10 M solution of hypochlorous acid, $K_a = 3.5 \times 10^{-8}$?

In tackling this problem, first note that the K_a is a small number, meaning hypochlorous acid is a weak acid.
To begin the problem, write down the equilibrium involved:

$$HOCl + H_2O = H_3O^+ + OCl^-$$

The equilibrium may be expressed mathematically by setting the K_a equal to the mass action expression:

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]}$$

Next, use the equilibrium to establish a table of initial conditions, change in equilibrium and final equilibrium conditions.

Initially, the HOCl concentration is 0.10 M, the concentrations of H_3O^+ and OCl^- are zero:

	$HOCl$	+	H_2O	=	H_3O^+	+	OCl^-
Initial	0.10 M				0		0
Change							
Equilibrium							

Note: Water will not be included in the calculation since is the solvent.

In order for equilibrium to be established, some of HOCl must dissociate and form H_3O^+ and OCl^-.

Since it is not known how much will dissociate, we'll call the amount of HOCl lost **-x** and the amount of H_3O^+ and OCl^- formed **+x**:

	$HOCl$	+	H_2O	=	H_3O^+	+	OCl^-
Initial	0.10 M				0		0
Change	-x				+x		+x
Equilibrium							

The above operation is justified by LeChatlier's Principle, which states: *<u>if a stress is places on an equilibrium, the equilibrium will shift in the direction which will relieve the stress</u>*.

In this case, the stress is **<u>the lack of H_3O^+ and OCl^-</u>** so the equilibrium will *<u>shift to the right</u>* to relieve the stress by forming some H_3O^+ and OCl^-.

By summing the initial concentrations and the change in concentrations, you can obtain the amount of each species at equilibrium:

	$HOCl$	+	H_2O	=	H_3O^+	+	OCl^-
Initial	0.10 M				0		0
Change	-x				+x		+x
Equilibrium	0.10 - x				+x		+x

These quantities will be used in the mass action expression for the equilibrium of the acid, as shown below.

The K_a for HOCl is 3.5×10^{-8}.

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{(x)(x)}{0.10 - x} = 3.5 \text{ x } 10^{-8}$$

The solution for **x** becomes simplified because the x shown in bold can be neglected. This **x** can be neglected because it will be negligibly small compared to the concentration, 0.10 M.

To determine whether x is negligible, compare the magnitude of the last decimal place of the concentration of the acid to the magnitude of the equilibrium constant. If the difference in magnitude is greater than 100, the x may be neglected.

In this case, the concentration is known to the 10^{-2} place and the equilibrium constant is the magnitude of 10^{-8}. The difference in magnitude is 10^{6}, therefore, x may easily be neglected. This simplifies the equation to:

$$\frac{(x)(x)}{0.10} = 3.5 \times 10^{-8}$$

Multiplying both sides by 0.10 yields:

$$x^2 = 3.5 \times 10^{-9}$$

Taking the square root of both sides yields:

$$x = [H_3O^+] = 5.9 \times 10^{-5} = [OCl^-] \text{ (also)}$$

To find the pH, take the negative log of the hydronium ion concentration:

$$pH = -\log[H_3O^+] = -\log(5.9 \times 10^{-5}) = 4.23$$

Incidently, the concentration of HOCl at equilibrium would be:

$$[HOCl] = 0.10 - 5.9 \times 10^{-5} = 0.10 \text{ M} \quad \text{(2 significant figures)}$$

This shows our assumption that x was negligible was valid.

A typical weak base problem may read:

What is the hydroxide ion concentration and pH of a 0.10 M solution of NH_3, $K_b = 1.8 \times 10^{-5}$?

Again, note that K_b is small. We will follow the same format as we used for weak acid solutions :

	NH_3	+	H_2O	=	NH_4^+	+	OH^-
Initial	0.10 M				0		0
Change							
Equilibrium							

We are assuming that before equilibrium is established, no NH_4^+ or OH^- have formed.

To establish equilibrium, a shift to the right has to occur. Since the amount of NH_3 lost, and the amounts of NH_4^+ and OH^- formed are not known, we assign the value of -x and +x, respectively:

	NH_3	$+ \; H_2O \; =$	NH_4^+	$+$	OH^-
Initial	0.10 M		0		0
Change	-x		+x		+x
Equilibrium					

By summing the initial concentrations and change in concentrations, we have the algebraic amount of each species in solution at equilibrium:

	NH_3	$+ \; H_2O \; =$	NH_4^+	$+$	OH^-
Initial	0.10 M		0		0
Change	-x		+x		+x
Equilibrium	0.10 - x		+x		+x

These quantities will be used in the mass action expression:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{0.10 - x} = 1.8 \times 10^{-5}$$

<u>Let's see if we can neglect the x in the denominator.</u>

The last decimal place in 0.10 is to the magnitude of10^{-2}.

The magnitude of the constant is 10^{-5}. --> <u>The difference in magnitude is 10^3</u>.

Since this difference is greater than 100, the x may be neglected. This simplifies the mathematical expression to:

$$\frac{(x)(x)}{0.10} = 1.8 \times 10^{-5}$$

Multiplying both sides of the equation by the denominator yields:

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

Taking the square root of both sides yields:

$$x = [NH_4^+] = [OH^-] = 1.3 \times 10^{-3}$$

To find the pH, first find the pOH by taking the negative log of the hydroxide ion concentration:

$$pOH = -\log[OH^-] = -\log(1.3 \times 10^{-3}) = 2.87$$

Then subtract the pOH from 14 to find the pH:

$$pH = 14.00 - pOH = 14.00 - 2.87 = 11.13$$

Buffer Problems

Buffer solutions consist of a weak acid and its conjugate base (acidic buffer) or a weak base and its conjugate acid (alkaline buffer). **They have the property of resisting pH change even when strong acid or strong base is introduced into solution**. *The way to recognize a buffer problem is to realize that both the concentration of the weak acid or base and their respective conjugate acid or base concentrations are known.* We'll go through an example of each type of buffer problem below.

Acidic Buffers

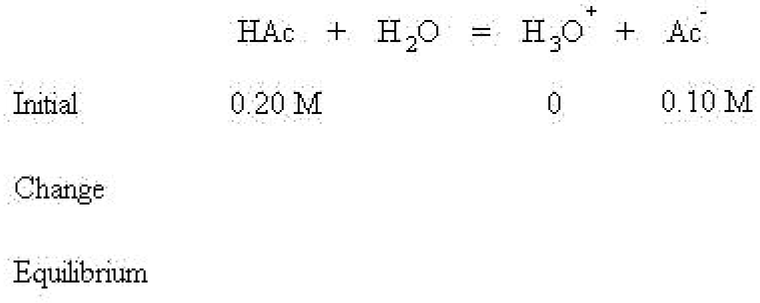
Suppose you have a solution which is 0.20 M in acetic acid (HAc) and 0.10 M in sodium acetate (NaAc). What will be the pH of this solution?

This is a typical buffer problem.

Notice that the concentrations of both the weak acid and its conjugate base are known.

The equilibrium is still that of acetic acid; the only difference is that we have a common ion (acetate ion) present.

First, set up a table as we have done before for a weak acid problem:

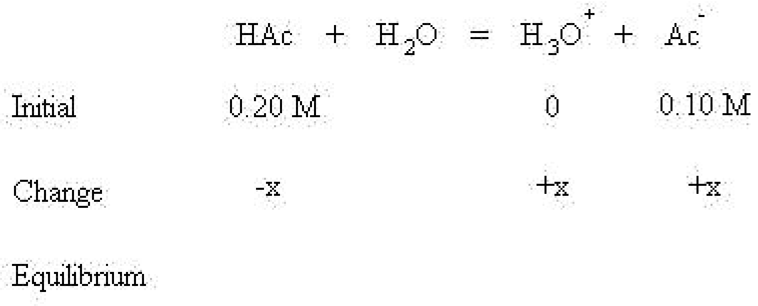


	HAc	+	H_2O	=	H_3O^+	+	Ac^-
Initial	0.20 M				0		0.10 M
Change							
Equilibrium							

Notice that the initial concentrations of both HAc and Ac^- are known. The acetate ion came from the sodium acetate.

The sodium ion is not a part of the equilibrium and is therefore neglected as a spectator ion.

In the next step we apply LeChatlier's principle and see that in order to establish equilibrium, some HAc will have to dissociate to produce hydronium ions:



	HAc	+	H_2O	=	H_3O^+	+	Ac^-
Initial	0.20 M				0		0.10 M
Change	-x				+x		+x
Equilibrium							

The concentrations of HAc, H_3O^+ and Ac^- at equilibrium will be the sum of initial concentrations and the change in concentrations:

	$HAc + H_2O$	$=$	H_3O^+	$+ Ac^-$
Initial	0.20 M		0	0.10 M
Change	-x		+x	+x
Equilibrium	0.20 -x		+x	0.10 + x

These algebraic quantities may now be inserted into the mass action equilibrium expression for acetic acid:

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} = \frac{(x)(0.10 + x)}{(0.20 - x)} = 1.8 \times 10^{-5}$$

The values of **x** shown above may often be neglected if they can be shown to be negligibly small.

Compare the concentrations to the K_a value. In this case the concentrations of the weak acid and its conjugate base are known to the 10^{-2} place and the K_a is to the 10^{-5} place.

Since the difference in magnitude is greater than 100 (actually 1000 times different), both of this x quantities may be neglected. This simplifies the algebraic expression to:

$$\frac{(x)(0.10)}{0.20} = 1.8 \times 10^{-5}$$

Solving for **x** gives the hydronium ion concentration:

$$x = [H_3O^+] = \frac{(1.8 \times 10^{-5})(0.20)}{0.10} = 3.6 \times 10^{-5}$$

To find the pH, take the negative log the hydronium ion concentration:

$$pH = -\log[H_3O^+] = -\log[3.6 \times 10^{-5}] = 4.44$$

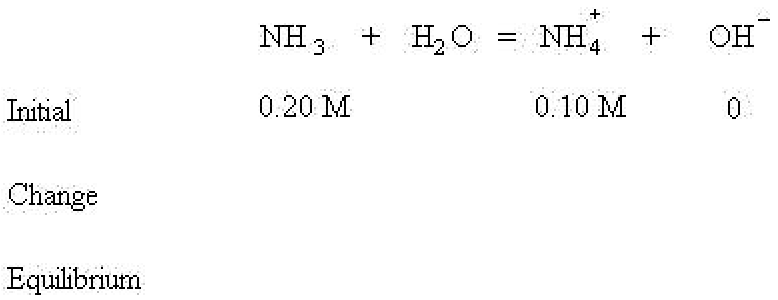
Alkaline Buffers

Suppose you have a alkaline buffer consisting of 0.20 M aqueous ammonia (NH_3) and 0.10 M ammonium chloride (NH_4Cl). What is the pH of the solution?

Notice that the concentrations of both the weak base and conjugate acid are known.

The ammonium ion is a common ion to the ammonia equilibrium. Chloride ion is not participating in the equilibrium (spectator ion) and will be ignored.

Begin by forming the table as we have with other acid\ base problems:

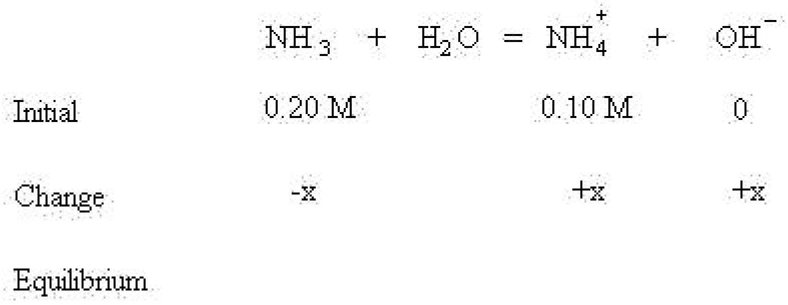


	NH_3	+	H_2O	=	NH_4^+	+	OH^-
Initial	0.20 M				0.10 M		0
Change							
Equilibrium							

Notice that the concentrations of both weak base and conjugate acid are known.

Apply LeChatlier's Principle and see that the equilibrium will shift to the right to create some OH^- to establish equilibrium.

This means some NH_3 will be lost and some additional NH_4^+ will be formed in addition to some OH^-.



	NH_3	+	H_2O	=	NH_4^+	+	OH^-
Initial	0.20 M				0.10 M		0
Change	-x				+x		+x
Equilibrium							

Sum the initial concentrations and the change in concentrations to find the amount of NH_3, NH_4^+ and OH^- at equilibrium:

	NH_3	+	H_2O	=	NH_4^+	+	OH^-
Initial	0.20 M				0.10 M		0
Change	-x				+x		+x
Equilibrium	0.20 - x				0.10 + x		+x

Insert the above expressions into the mass action equilibrium expression:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.10 + x)(x)}{(0.20 - x)} = 1.8 \times 10^{-5}$$

The **x** quantities shown above often may be neglected. i.e. compare the magnitude of the concentrations of NH_3 and NH_4^+ to the magnitude of K_b.

In this case the magnitudes of the concentrations are known to the 10^{-2} magnitude and the K_b is known to the 10^{-5} magnitude.

Since the difference in magnitude is greater than 100 (difference is 1000), the x quantities shown in bold may be neglected.

This simplifies the expression to the expression shown:

$$\frac{(0.10)(x)}{0.20} = 1.8 \times 10^{-5}$$

Solve this expression for x which will provide the hydroxide ion concentration:

$$x = [OH\ ] = \frac{(1.8 \times 10^{-5})(0.20)}{0.10} = 3.6 \times 10^{-5}$$

To find the pH, first find the pOH by taking the negative log of the hydroxide ion concentration:

$$pOH = -\log[OH^-] = -\log(3.6 \times 10^{-5}) = 4.44$$

Next, subtract the pOH from 14.00 to find the pH:

$$pH = 14.00 - pOH = 14.00 - 4.44 = 9.56$$

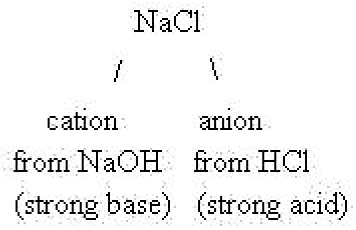
<u>Hydrolysis Problems</u>

Hydrolysis problems deal with the salts of weak acids and weak bases.

A salt may be defined as the product of an acid and a base. *The cation of the salt always comes from the base and the anion always comes from the acid* (keep the vowels and consonants together).

<u>Not all salts are neutral</u>. *Some salts will hydrolyze in water and produce either acidic or basic solutions.*

Let's see how this may occur. The salt, NaCl, will form a neutral solution--no hydrolysis occurs.

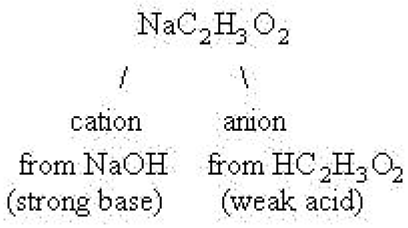


Since the sodium ion came from NaOH, a strong base, this ion is a **weak** conjugate acid and <u>will not hydrolyze</u>. - <u>It will float around in solution as a spectator ion.</u>

Likewise, the chloride ion came from HCl, a strong acid. That makes the chloride ion a **weak** conjugate base and it <u>will not hydrolyze</u>. <u>It also will float around in solution as a spectator ion.</u>

As a result, the only hydronium ions present in solution are due to the autoionization of water, and the solution will be neutral in pH.

Next, let us consider the salt, sodium acetate, whose concentration is 0.10 M:



The cation, sodium ion, came from a strong base, NaOH, and as discussed above, <u>will not hydrolyze</u>.

However, the anion, acetate ion, came from a weak acid, acetic acid. Acetate ion is therefore a **strong** conjugate base and <u>will hydrolyze</u>.

This means it will behave as a Lowry-Bronsted base, and accept a proton from water, as shown in the equilibrium below:

$$C_2H_3O_2^- + H_2O = HC_2H_3O_2 + OH^-$$

Notice that hydroxide ion is generated and the salt solution will be alkaline in pH.

To calculate the pH of the solution we need to know the initial concentration of the acetate ion (which will be given) and the value of the equilibrium constant, K_b (sometimes labeled as K_h, for hydrolysis constant).

The equilibrium constant may be calculated from the K_w of water and the K_a of the weak acid from which the conjugate base forms:

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Recall the concentration of the sodium acetate solution was given as 0.10 M.

The acetate ion concentration is also 0.10 M since every mole of sodium acetate contains 1 mole of acetate ions.

One can proceed to solve for the pH as we have done for other equilibrium problems. Begin by showing the equilibrium and the initial concentrations of species present:

	$C_2H_3O_2^-$	+	H_2O	=	$HC_2H_3O_2$	+	OH^-
Initial	0.10 M				0		0
Change							
Equilibrium							

According to LeChatlier's Principle, the reaction will *<u>shift to the right</u>* to establish equilibrium since there is no acetic acid or hydroxide yet present. This means an x amount of acetate ion will be consumed and an x amount of both acetic acid an hydroxide ion will be formed, as shown in the table below:

	$C_2H_3O_2^-$	+	H_2O	=	$HC_2H_3O_2$	+	OH^-
Initial	0.10 M				0		0
Change	-x				+x		+x
Equilibrium							

Sum the initial concentrations and the change in concentrations to find the amounts present at equilibrium:

	$C_2H_3O_2^-$	$+$	H_2O	$=$	$HC_2H_3O_2$	$+$	OH^-
Initial	0.10 M				0		0
Change	-x				+x		+x
Equilibrium	0.10 - x				+x		+x

These quantities may by substituted into the mass action expression:

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{(x)(x)}{(0.10 - x)} = 5.6 \times 10^{-10}$$

The **x** quantity shown in the denominator may be neglected since the difference in magnitude between the initial concentration of acetate ion (10^{-2}) and the equilibrium constant (10^{-10}) is 10^8.

This simplifies the above expression to:

$$K_b = \frac{(x)(x)}{0.10} = 5.6 \times 10^{-10}$$

Multiplying both sides of the equation by the denominator, 0.10, yields:

$$x^2 = 5.6 \times 10^{-11}$$

To find x, take the square root of both sides of the equation:

$$x = 7.5 \times 10^{-6} = [OH^-]$$

Notice that x corresponds to the hydroxide ion concentration. Now that the hydroxide ion concentration is known, the pH may be found by first calculating the pOH:

$$pOH = -\log[OH^-] = -\log(7.5 \times 10^{-6}) = 5.12$$

The pH may now be found by subtracting the pOH from 14.00:

$$pH = 14.00 - pOH = 14.00 - 5.12 = 8.88$$

As shown by the equilibrium, the solution is alkaline.

Now, suppose one had a 0.10 M solution of NH_4Cl. What would be the pH of this solution?

First consider if any hydrolysis will take place.

NH_4Cl
/ \
cation anion
from NH_3 from HCl
(weak base) (strong acid)

The chloride anion is the **weak** conjugate base of a strong acid (HCl) and will not hydrolyze.

The ammonium cation, however, is the **strong** conjugate acid of a weak base (NH_3) and will hydrolyze--it will act as a Lowry-Bronsted acid and donate a proton to water:

$$NH_4^+ + H_2O = NH_3 + H_3O^+$$

Since hydronium ion is being generated, this solution will be acidic in pH.

To calculate the pH of this solution, we need to know the initial concentration of the salt (which will be given), and the equilibrium constant.

The equilibrium constant will be calculated in a similar manner as for alkaline salts, using the K_w of water in the K_b of the base from which the conjugate acid formed:

$$K_a = \frac{K_w}{K_b} = \frac{1 \text{ x } 10^{-14}}{1.8 \text{ x } 10^{-5}} = 5.6 \text{ x } 10^{-10}$$

Using an initial concentration of salt to be 0.10 M, set up a table of initial concentrations, change in concentrations and equilibrium concentrations:

	NH_4^+	+	H_2O	=	NH_3	+	H_3O^+
Initial	0.10 M				0		0
Change							
Equilibrium							

We are assuming that before equilibrium is established, no ammonia or hydronium ion has been produced.

In order to establish equilibrium, an **x** amount of ammonium ion will be lost to form an **x** amount of ammonia and hydronium ion.

This follows LeChatlier's Principle--the reaction will **shift to the right** to establish equilibrium. The change in concentrations is shown below:

	NH_4^+	+	H_2O	=	NH_3	+	H_3O^+
Initial	0.10 M				0		0
Change	-x				+x		+x
Equilibrium							

Sum the initial concentrations and change in concentrations to find the concentrations present at equilibrium:

	NH_4^+	+	H_2O	=	NH_3	+	H_3O^+
Initial	0.10 M				0		0
Change	-x				+x		+x
Equilibrium	0.10 - x				+x		+x

Use the equilibrium concentrations in the mass action expression:

$$K_a = \frac{[NH_3][H_2O\ ]}{[NH_4^+]} = \frac{(x)(x)}{0.10 - x} = 5.6 \times 10^{-10}$$

The x amount shown in bold may be neglected since the difference in magnitude between the initial concentration (10^{-2}) and the equilibrium constant (10^{-10}) is 10^8. This simplifies the above expression to:

$$K_a = \frac{(x)(x)}{0.10} = 5.6 \times 10^{-10}$$

Multiplying both sides of the equation by the denominator, 0.10, yields:

$$x^2 = 5.6 \times 10^{-11}$$

Solve for x by taking the square root of both sides of the equation:

$$x = [H_3O^+] = 7.5 \times 10^{-6}$$

Notice that x is also the hydronium ion concentration. To find the pH take the negative log of the hydronium ion concentration:

$$pH = -\log[H_3O^+] = -\log(7.5 \times 10^{-6}) = 5.12$$

As shown by the equilibrium, the solution is acidic.