

## Acid-Base Equilibrium

### Solving pH Problems for Weak Acids and Bases

How do we classify a compound as an acid or base? Recall that the word **acid** is from the Latin word *acidus* which means sour. The word **alkali** is an Arabic word for the ashes that come from burning certain plants and water solutions of these materials feel slippery and taste bitter. (Of course, you should *never* taste chemicals in the laboratory.) In this activity, we explore several different kinds of equilibrium constants,  $K$ . We will discuss  $K_a$ ,  $K_b$ , and  $K_w$ . But, first it is important that we do a quick review of general acid-base theory. There are three major acid-base theories and you should know each by name:

#### ARRHENIUS THEORY

**acid**—a substance that produces a proton ( $H^+$ ) in water forming the hydronium ion,  $H_3O^+$  in aqueous solutions

**base**—a substance that produces an hydroxide ion in water ( $OH^-$ ); note that ammonia is a MAJOR exception since it is a base, but has no  $OH^-$  to produce!

#### BRÖNSTED-LOWRY THEORY

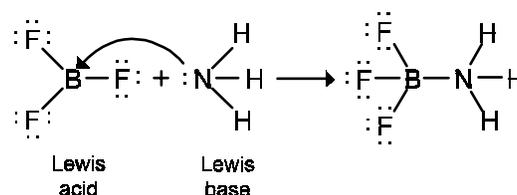
**acid**—a substance that produces a proton ( $H^+$ ) in water forming the hydronium ion,  $H_3O^+$  in aqueous solutions

**base**—a substance that accepts a proton in water; this better explains the basic behavior of ammonia since  $NH_3 + H^+ \rightleftharpoons NH_4^+$ , the ammonium ion in aqueous solutions

#### LEWIS THEORY

**acid**—a substance that accepts an electron pair into an empty orbital (think “acids accept”);  $BF_3$  is the classic example of a Lewis acid.

**base**—a substance that donates an electron pair.



Additional acid-base terms to know:

**monoprotic**—describes acids donating one  $H^+$  such as  $HCl$ ,  $HC_2H_3O_2$ , or  $HNO_3$

**diprotic**—describes acids donating two  $H^+$  ions such as  $H_2SO_4$

**polyprotic**—describes acids donating more than one  $H^+$  ions such as  $H_3PO_4$

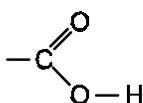
**amphiprotic**—describes a substance that can act as either an acid or a base. This means it can either lose a proton or gain one. Water can do this to form hydroxide or hydronium ions. Other examples include  $HCO_3^-$ ,  $HSO_4^-$ ,  $HPO_4^{2-}$

**amphoteric**—describes an oxide that shows both acidic and basic properties. Soluble aluminum compounds are famous for this behavior.

**ACID-BASE DISSOCIATION CONSTANTS**

IF an acid or base is strong, it completely dissociates and we assume the reaction goes to completion. IF an acid or base is weak, it does not dissociate completely and equilibrium is established. *The vast majority of acids and bases are weak.* Their equilibrium constants,  $K$ , are referred to as acid or base dissociation constants,  $K_a$  and  $K_b$  respectively. You will have to use the  $K_a$  or  $K_b$  to determine the pH in an equilibrium problem, or vice versa.

Many common weak acids are oxyacids, like phosphoric acid and nitrous acid. Other common weak acids are organic acids—those that contain a carboxyl group,  $-\text{COOH}$ , like acetic acid and benzoic acid. Acetic acid is written  $\text{HC}_2\text{H}_3\text{O}_2$  or  $\text{CH}_3\text{COOH}$  or  $\text{H}_3\text{CCOOH}$  if you really want to emphasize the bonding. It simply means a methyl [ $-\text{CH}_3$ ] group is attached to the carboxylic acid group shown below.



The generalized chemical reaction showing the dissociation of a weak acid is:



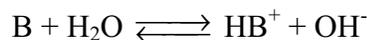
“A<sup>-</sup>” is the anion of the acid, which is whatever remains once the proton is removed. It is important to remember that  $K$  is a relationship (the equilibrium expression) and a number. For weak acids, the number is much less than one since the equilibrium position is FAR to the left.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \lll 1$$

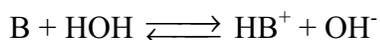
There is no need to memorize any  $K_a$  values.

Weak bases that are not Arrhenius bases (without  $\text{OH}^-$ ) react with water to produce a hydroxide ion. Common examples of weak non-Arrhenius bases are ammonia ( $\text{NH}_3$ ), methylamine ( $\text{CH}_3\text{NH}_2$ ), and ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ ). The lone pair of electrons on N forms a bond with  $\text{H}^+$ . Most weak bases involve N. No need to memorize these, just have an awareness.

The generalized chemical reaction showing the dissociation of a weak base is:



You may want to write the water as  $\text{HOH}$ , so that it is easier to see that the base is accepting a proton and leaving the hydroxide ion behind.



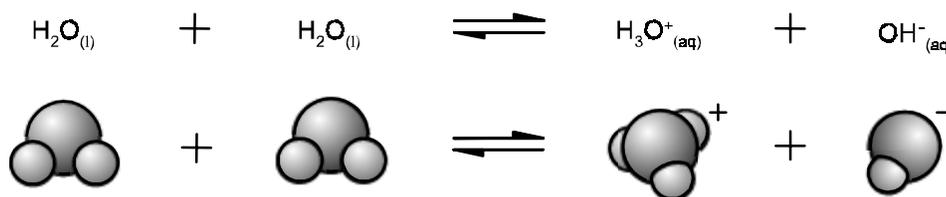
The equilibrium expression for the dissociation of a weak base is known as the  $K_b$ .

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \lll 1$$

### THE SIGNIFICANCE OF $K_w$

Around 1900 a man named Fredrich Kohlrausch found that no matter how pure a sample of water, it still conducts a minute amount of electric current. In order to do this water must be able to self-ionize.

The water molecule is **amphiprotic**, meaning it can behave as either an acid or a base. It may dissociate with itself to a slight extent. *Only about 2 out of a billion water molecules are ionized at any instant!*



The equilibrium expression for the above reaction is referred to as  $K_w$ , **the ionization constant for water**.  $K_w$  is also the relationship between the acid and base dissociation constants of a conjugate acid-base pair.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = K_a \times K_b = 1.0 \times 10^{-14} \quad @ 25^\circ\text{C}$$

### THE PH SCALE

$K_w$  is the entire basis for the pH scale. The scale is really intended to communicate the strengths of weak acids and bases. The pH of a solution is calculated as the negative base 10 logarithm of the hydronium ion concentration or simply the  $[\text{H}^+]$ :

$$\text{pH} = -\log [\text{H}^+] \quad \text{which also means that } [\text{H}_3\text{O}^+] \text{ or } [\text{H}^+] = 10^{-\text{pH}}$$

Since  $K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$  and a pure sample of water has  $[\text{H}^+] = [\text{OH}^-]$  and each is equal to  $1 \times 10^{-7}$ , we can now account for the fact that the pH of a neutral solution is 7 and that the range of the entire scale is 0-14.

$$\begin{array}{ccccc} \text{most acidic} & & \text{neutral} & & \text{most basic} \\ 0 & \leftarrow & 7.0 & \rightarrow & 14 \end{array}$$

If more hydrogen ion is present,  $[\text{H}^+] > [\text{OH}^-]$ , and the pH is acidic (less than 7). If more hydroxide ion is present,  $[\text{H}^+] < [\text{OH}^-]$ , and the pH is basic (greater than 7).

The pOH of a solution is calculated as the negative base 10 logarithm of the hydroxide ion concentration:

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

and best yet,  $\text{pH} + \text{pOH} = 14$

The pH scale is a logarithmic scale which means that a difference of two units (an acid with a pH of 3 versus a pH of 5) is a difference of  $10^2$  units, or 100, in terms of the strength of the acid or base. So, an acid with a pH 3 is 100 times more acidic than an acid with a pH of 5. Logarithmic numbers have a characteristic and a mantissa. The characteristic is the part to the left of the decimal while the mantissa is the part to the right of the decimal. The characteristic is a place holder while the mantissa is communicating the accuracy of the measurement. For this reason, the decimal places communicate the significant figures. If you are given a pH of 3.58 in a problem and are asked to solve for the concentration of the weak acid, you should report its concentration to two significant figures. Conversely, if you are asked to find the pH of a weak base and given its concentration as 1.25M, then you should report the pH with three decimal places EVEN if it comes out to be something like 10.565.

### CALCULATING THE PH OF ACIDS AND BASES

First, determine if the acid or base in the question is strong or weak. If it is strong, take the negative log of the acid or base concentration to calculate either the pH or pOH. If it is weak, you enter the land of equilibrium problems and a RICE table is in order. Always start by writing the balanced equation, setting up the acid equilibrium expression ( $K_a$ ), or the base equilibrium expression ( $K_b$ ), and defining initial concentrations, changes, and final concentrations in terms of “ $x$ ”. Once you have done this substitute values and variables into the  $K_a$  or  $K_b$  expression and solve for “ $x$ ”.

#### Example 1

Calculate the pH of a 0.015 M HCl solution.

**Solution:** Since this is a strong acid go directly to  $\text{pH} = -\log [\text{H}^+] = -\log [0.015] = 1.82$  (two significant figures given for the concentration requires two decimal places on the pH)

#### Example 2

The  $K_a$  of acetic acid is  $1.8 \times 10^{-5}$ . (a) Calculate the pH of a  $1.5 \times 10^{-3}$  M solution of acetic acid. (b) What is the equilibrium concentration of acetic acid?

#### Solution:

(a) Since this is a weak acid, a RICE table is in order.

Reaction	$\text{HC}_2\text{H}_3\text{O}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	$1.5 \times 10^{-3}$		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$(1.5 \times 10^{-3} - x)$		$x$		$x$

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{[x^2]}{[1.5 \times 10^{-3} - x]} = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} (1.5 \times 10^{-3} - x) = x^2$$

Set the equation equal to zero so that  $x^2$  is positive.

$$0 = x^2 + 1.8 \times 10^{-5}x - 2.7 \times 10^{-8}$$

Solve using the quadratic formula. It is recommended that you use a graphing calculator with a quadratic formula solving program since you are allowed to do that on the AP Chemistry exam.

$$x = [\text{C}_2\text{H}_3\text{O}_2^-] = [\text{H}^+] = 1.6 \times 10^{-4}$$

$$\therefore \text{pH} = -\log[\text{H}^+] = -\log [1.6 \times 10^{-4}] = 3.80$$

(2 decimal places since 2 significant digits in the original concentration)

$$(b) [\text{HC}_2\text{H}_3\text{O}_2] \text{ at equilibrium} = 1.5 \times 10^{-3} - x = 1.5 \times 10^{-3} - 1.6 \times 10^{-4} = 1.3 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

Notice that we had to use the quadratic formula. Many equilibrium problems allow you to “neglect  $x$ ” which greatly simplifies the calculation and avoids the quadratic formula all together. *You may always neglect subtracting  $x$  when the original concentration of the weak acid or base is greater than  $100K_a$  or  $100K_b$ .*

Examine Example 1 again. If our original concentration had been something like 0.15M, then we could have neglected subtracting  $x$  since  $100K_a = 1.8 \times 10^{-3} = 0.0018$  and  $0.15 > 0.0018$ .

The determination of the pH of a **weak base** is very similar to the determination of the pH of a weak acid. Follow the same steps. Remember, however, that  $x$  is the **[OH]** and taking the negative log of  $x$  will give you the **pOH** and not the pH! Then use the relationship that  $\text{pH} + \text{pOH} = 14$ .

### Example 3

Calculate the pH of a 1.0 M solution of methylamine,  $\text{CH}_3\text{NH}_2$  ( $K_b = 4.38 \times 10^{-4}$ ).

**Solution:** Since this is a weak base, again a RICE table is in order. Remember to determine if you can “neglect  $x$ ”, just be sure and indicate in your work that you at least thought about “ $x$ ” by crossing  $x$  out and writing “neglect  $x$ ”. Also, with bases that do NOT contain an  $\text{OH}^-$  ion, it is easier to write a correct equation if you include the water and even write it as HOH.

Reaction	$\text{CH}_3\text{NH}_2$	+	$\text{HOH}_{(l)}$	$\rightleftharpoons$	$\text{OH}^-$	+	$\text{CH}_3\text{NH}_3^+$
Initial	1.0 M				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$(1.0 - x)$				$x$		$x$

$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]} = \frac{[x^2]}{[1.00 - x]} = \frac{[x^2]}{[1.00]} = 4.38 \times 10^{-4} \quad \text{Then solve for "x"}$$

“neglect x”

$$x = \sqrt{(4.38 \times 10^{-4})(1.00)} = 0.0209$$

$$x = [\text{OH}^-] \text{ from our table above so, } \text{pOH} = -\log [0.0209] = 1.68$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.68 = 12.32$$

### CALCULATING PERCENT DISSOCIATION

Ah, this is the easy part! It's simply the  $\left[ \frac{\text{amount dissociated}}{\text{original concentration}} \right] \times 100\%$ .

To find the percent dissociated from Example 1, recall that  $x = [\text{H}^+]$  which indicates the “amount dissociated” so...

$$\% \text{ dissociation} = \left( \frac{\text{amount dissociated}}{\text{original concentration}} \right) \times 100\% = \left( \frac{1.6 \times 10^{-4}}{1.5 \times 10^{-3}} \right) \times 100\% = 10.7\%$$

We can also calculate  $K_a$  from percent dissociation.

#### Example 4

In a 0.100 M aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of  $K_a$  for this acid.

**Solution:** If an acid is 3.7 % dissociated, then

$$3.7\% = \left( \frac{\text{H}^+ \text{ dissociated}}{\text{original concentration}} \right) \times 100\%; \text{ first divide both sides by 100}$$

$$0.037 = \left( \frac{\text{H}^+ \text{ dissociated}}{0.100 \text{ M}} \right) \text{ so, } (0.037)(0.100\text{M}) = 0.0037\text{M} = [\text{H}^+]$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[x^2]}{[0.100 - x]} = \frac{[0.0037^2]}{[0.100]} = 1.4 \times 10^{-4}$$

**PURPOSE**

You will be introduced to the concept of weak acid-base equilibrium. You will learn to solve acid-base equilibrium problems using the RICE table problem-solving method and subsequently calculate the pH of the resulting solution.

**MATERIALS**

calculator

paper and pencil

**PROCEDURE**

Solve the problems found on your student answer page. Be sure to show all work paying attention to the proper use of significant digits and units.

Name \_\_\_\_\_

Period \_\_\_\_\_

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### Solving pH Problems for Weak Acids and Bases

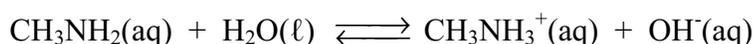
#### CONCLUSION QUESTIONS

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Use your own paper and show all work and pay special attention to significant digits and units where appropriate.

1. A dilute solution of household ammonia contains 0.3124 mol of  $\text{NH}_3$  per liter of solution. The  $K_b$  of ammonia is  $1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ .
  - (a) Calculate the hydroxide ion concentration of the solution at  $25^\circ\text{C}$ .
  - (b) Calculate the pH of the solution at  $25^\circ\text{C}$ .
2. (a) Calculate the ionization constant for HF if a 0.10M solution of HF is 8.1% ionized at  $25^\circ\text{C}$ .
  - (b) Calculate the pH of the solution.
3. Formic acid is the irritant that causes the body's reaction to an ant's sting. It has a  $K_a$  value of  $1.8 \times 10^{-4}$  at  $25^\circ\text{C}$ .
  - (a) Calculate the concentration of hydrogen ion in a 0.575M solution at  $25^\circ\text{C}$ .
  - (b) Calculate the percent ionization of a 0.575M solution at  $25^\circ\text{C}$ .
4. Acetic acid has a  $K_a$  value of  $1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ .
  - (a) Calculate the percent ionization of a 0.265M acetic acid solution at  $25^\circ\text{C}$ .
  - (b) Calculate the  $[\text{OH}^-]$  of the solution at  $25^\circ\text{C}$ .
5. Monochloroacetic acid,  $\text{HC}_2\text{H}_2\text{ClO}_2$ , is a skin irritant that is used in "chemical peels" intended to remove the top layer of dead skin from the face and ultimately improve the complexion. The value of the  $K_a$  for monochloroacetic acid is  $1.35 \times 10^{-3}$ .
  - (a) Calculate the pH of a 0.25M solution of monochloroacetic acid at  $25^\circ\text{C}$ .
  - (b) Calculate the percent ionization of a 0.25M solution of monochloroacetic acetic acid at  $25^\circ\text{C}$ .

6. Codeine ( $C_{18}H_{21}NO_3$ ) is a derivative of morphine that is used as an analgesic, narcotic or antitussive. It was once commonly used in cough syrups but is now available only by prescription because of its addictive properties.
- (a) If the pH of a  $6.3 \times 10^{-3}$  M solution of codeine is 9.83 at  $30^\circ\text{C}$ , calculate the  $[\text{H}^+]$  of the solution.
- (b) Calculate the  $K_b$  at  $30^\circ\text{C}$ .
7. The  $K_a$  of acetic acid at  $25^\circ\text{C}$  is  $1.8 \times 10^{-5}$ .
- (a) What are the equilibrium concentrations of  $\text{H}_3\text{O}^+$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$  and  $\text{HC}_2\text{H}_3\text{O}_2$  in a 0.350 M aqueous solution of acetic acid?
- (b) What is the pH of the solution at  $25^\circ\text{C}$ ?
8. The weak base methylamine,  $\text{CH}_3\text{NH}_2$ , has a  $K_b$  of  $4.2 \times 10^{-4}$  at  $25^\circ\text{C}$ . It reacts with water according to the equation



- (a) Calculate the equilibrium concentration of  $\text{OH}^-$  in a 0.15M solution of the base.
- (b) What are the pH and pOH of the solution?
9. A 1.00 M solution of a weak acid has a pH of 3.849 at  $25^\circ\text{C}$ .
- (a) Calculate the  $[\text{H}^+]$  in the 1.00 M solution.
- (b) Calculate the  $K_a$  for the weak acid at  $25^\circ\text{C}$ .
10. Phosphoric acid has a  $K_{a1}$  of  $7.5 \times 10^{-3}$  at  $25^\circ\text{C}$ .
- (a) Calculate the  $[\text{H}_2\text{PO}_4^{2-}]$  present at equilibrium in a 0.35 M solution.
- (b) Calculate the pH of the solution at  $25^\circ\text{C}$ .