

Chem 116 POGIL Worksheet - Week 9

Introduction to Acid-Base Concepts

Why?

Acids and bases are important substances in many settings. In everyday life we encounter acids such as vinegar and lemon juice and bases such as ammonia and lye in drain cleaners. Many important processes in chemistry and biology involve reactions of acids with bases. Acid-base reactions can be understood in terms of the transfer of hydrogen ion, and the concentration of hydrogen ion in a reaction mixture, measured as pH, is often an important factor in how reactions occur.

Learning Objectives

- Understand the Brønsted-Lowry theory of acids and bases
- Understand the concepts of conjugate acid-base pairs
- Understand the role of solvent protolysis in acid-base chemistry
- Understand the concept of K_w for water and how it relates to the definition of pH and pOH
- Understand the concept of K_a for a weak acid

Success Criteria

- Be able to analyze acid-base reactions in terms of conjugate acid-base pairs and proton transfer
- Be able to write the formula of an acid's conjugate base or a base's conjugate acid
- Be able to use K_w to calculate concentrations of H_3O^+ and OH^- in acidic or basic solutions
- Be able to calculate pH and pOH
- Be able to calculate concentrations of hydronium ion and hydroxide ion in solutions of pure strong acid or strong base in water
- Be able to use K_a to calculate the concentrations of all species present in a solution of a pure weak acid in water

Prerequisite

Have read Sections 16.1-16.6

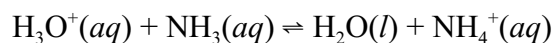
Information (Brønsted-Lowry Theory)

In the Arrhenius theory, an acid is a substance that produces H^+ ion in solution, and a base is a substance that produces OH^- ion in solution. This theory is only useful for aqueous (water) solutions. In 1923, Brønsted (Danish) and Lowry (English) independently proposed a new theory that could be applied to other solvent systems. The Brønsted-Lowry Theory use the following definitions:

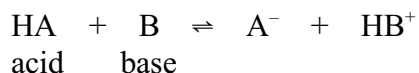
Acid - a substance that donates protons (H^+)

Base - a substance that accepts protons (H^+)

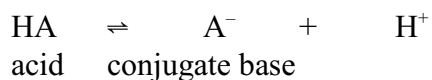
In this theory, acid-base reactions are seen as proton transfer reactions. For example, consider the reaction between the hydronium ion and ammonia in water:



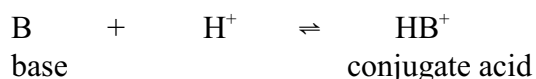
This involves transfer of a proton from the hydronium ion to the ammonia molecule to produce water and the ammonium ion. This makes H_3O^+ an acid and NH_3 a base. In general terms, all Brønsted-Lowry acid-base reactions fit the general pattern



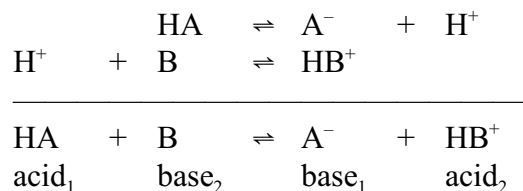
When an acid, HA, loses a proton it becomes its **conjugate base**, A^- , a species capable of accepting a proton in the reverse reaction.



Likewise, when a base, B, gains a proton, it becomes its **conjugate acid**, BH^+ , a species capable of donating a proton in the reverse reaction.



The Brønsted-Lowry concept of conjugate acid base pairs leads to the idea that all acid-base reactions are proton transfer reactions. The generic reaction between an acid HA and a base B can be viewed as



Species with the same subscripts are a conjugate acid-base pairs.

Key Questions

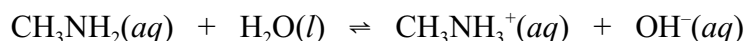
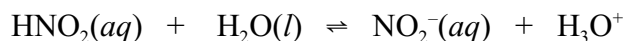
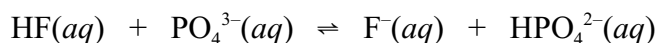
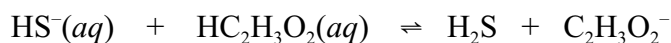
- In the spaces provided, write the formulas of the conjugate bases of the given Brønsted-Lowry acids.

Acid	HNO_3	NH_4^+	HSO_4^-	H_2SO_4	$\text{HC}_2\text{H}_3\text{O}_2$
Conjugate base					

2. In the spaces provided, write the formulas of the conjugate acids of the given Brønsted-Lowry bases.

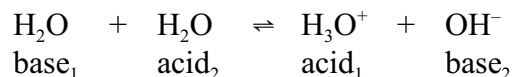
Base	OH^-	NH_3	HS^-	SO_4^{2-}	CH_3NH_2
Conjugate acid					

3. Using the notation acid₁/base₁ and base₂/acid₂ (as shown above), identify the Brønsted-Lowry conjugate acid-base pairs in the following reactions.



Information (Water's Autoprotolysis)

Pure water has an equilibrium with H_3O^+ and OH^- called **autoprotolysis** or **autodissociation**.



for which we might write the following equilibrium expression:

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

We omit the concentration of $\text{H}_2\text{O}(l)$ from the expression, because it is a pure liquid. We can also ignore the concentration of H_2O for dilute solutions, because $[\text{H}_2\text{O}]$ is virtually constant. At a temperature of 25 °C K_w has a measured value of 1.0×10^{-14} :

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ M}^2 \text{ at } 25^\circ\text{C}$$

K_w is called the **ion product** or **dissociation constant** of water. The units on K_w are generally not written, but they are implicitly M^2 , as shown above.

For pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$. To find the value of this concentration, let $x = [\text{H}_3\text{O}^+] = [\text{OH}^-]$ and substitute into the ion product expression for water:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} = x^2$$

$$x = 1.0 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

This condition of $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ defines **neutral water**.

The K_w expression must be obeyed for any dilute solution in water. Suppose we add a strong acid, such as HCl, which dissociates completely into H_3O^+ and Cl^- ions. This will increase $[\text{H}_3\text{O}^+]$ in the solution, but by LeChatelier's Principle it will cause the autoprotolysis equilibrium to shift left to maintain $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$. This will cause $[\text{OH}^-]$ to become smaller as more molecular H_2O is formed in response to the stress of excess H_3O^+ ion in the solution. A strong base, such as NaOH, which dissociates completely into Na^+ and OH^- ions, would have the reverse effect. This will increase $[\text{OH}^-]$ in the solution, but it will make $[\text{H}_3\text{O}^+]$ smaller as the autoprotolysis equilibrium shifts left to maintain $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$. In general, owing to these shifts in the autoprotolysis equilibrium, a solution is acidic if $[\text{H}_3\text{O}^+] > 10^{-7} \text{ M}$ and $[\text{OH}^-] < 10^{-7} \text{ M}$, and a solution is basic if $[\text{H}_3\text{O}^+] < 10^{-7} \text{ M}$ and $[\text{OH}^-] > 10^{-7} \text{ M}$.

Key Questions

4. Given the following concentrations of H_3O^+ or OH^- , calculate the concentration of OH^- or H_3O^+ , and indicate whether the solution is acidic or basic.

$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	Acidic or basic?
	$1.0 \times 10^{-5} \text{ M}$	
	$4.0 \times 10^{-9} \text{ M}$	
$1.2 \times 10^{-8} \text{ M}$		

Information (pH and pOH)

It is often convenient to express $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ by the logarithmic terms **pH** and **pOH**, respectively, defined as

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

Note that the symbol "p" in front of any quantity means "negative base-10 logarithm of"; e.g., $\text{p}K_w = -\log K_w$. The relationship between pH and pOH can be derived from K_w .

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Taking base-10 logarithms of both sides of this equation, we have

$$\log K_w = \log[\text{H}_3\text{O}^+][\text{OH}^-] = \log[\text{H}_3\text{O}^+] + \log\{\text{OH}^-\} = -14.00$$

Changing the sign across this equation, we have

$$-\log K_w = -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] = 14.00$$

If we now recognize that the negative logarithm of any quantity X can be designated with the symbol pX, then this equation becomes

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

For neutral water, where $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$, $\text{pH} = \text{pOH} = 7.00$. For acidic solutions pH is less than 7, and for basic solutions pH is greater than 7. Note that pOH runs in the opposite sense. For acid solutions pOH is greater than 7, and for basic solutions pOH is less than 7. It is possible to have solutions in which pH or pOH are greater than 14 or less than 0 (i.e., negative).

Note that the number of decimal places in a logarithm indicates the number of significant figures in the original number. For example, the base-10 logarithm of 1.45×10^{-15} (3 sig. figs.) is -14.839 , where the decimal part indicates the three significant figures. The -14 part (left of the decimal) relates to the power of ten, and has no relevance to significant figures. Why is this? Because we cannot take the logarithm of a negative decimal number, the logarithm -14.839 is actually the sum of a negative integer (-15) and a positive decimal (0.161); i.e., $-15 + 0.161 = -14.839$. The -15 , called the *characteristic*, relates to the 10^{-15} of the original number, and the 0.161 , called the *mantissa*, relates to the 1.45 of the original number, which is where the significant digits are. *Be sure when calculating pH or pOH that the number of decimal places matches the number of significant figures in the number.*

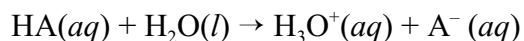
Key Questions

- Complete the following table by calculating the missing entries and indicate whether the solution is acidic or basic. Be sure your answers are expressed to the proper number of significant figures.

$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	pH	pOH	acidic or basic?
$5.8 \times 10^{-5} \text{ M}$				
	$6.2 \times 10^{-6} \text{ M}$			
		11.24		
			9.70	
2.0 M				

Information (Solutions of Strong Acids and Bases)

When a strong acid, HA, dissolves in water it dissociates completely into H_3O^+ and A^- ions, leaving no molecular HA in the solution:



Thus, when we talk about the concentration of a strong acid solution, say 0.10 M HCl, we are usually referring to the number of moles per liter used to make the solution, not what is actually present in the solution. Because of dissociation, there is virtually no molecular HCl in a 0.10 M HCl solution! We can define the *analytical concentration* of the acid HA, symbolized C_{HA} , as the number of moles per liter of acid used to make the solution. Thus, for 0.10 M HCl, $C_{\text{HCl}} = 0.10 \text{ M}$. Then, using bracket symbols, we can refer to actual concentrations in the solution as $[\text{HA}]$, $[\text{H}_3\text{O}^+]$, and $[\text{A}^-]$. For moderate analytical concentrations of strong acid ($C_{\text{HA}} \gg 10^{-7} \text{ M}$), we can generally assume that the acid's dissociation supplies virtually all the H_3O^+ in the solution; i.e., water's contribution is insignificant. For a given analytical concentration of a pure strong acid at moderate concentration, we would have the following values initially and after dissociation:

	$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$		
Initial	C_{HA}	~ 0	0
After dissociation	~ 0	C_{HA}	C_{HA}

In other words, the concentrations of hydronium ion and conjugate base in the solution are equivalent to the number of moles per liter of acid added to make the solution; i.e., $[\text{H}_3\text{O}^+] = [\text{A}^-] = C_{\text{HA}}$. Because of complete dissociation, $[\text{HA}] = 0$. For 0.10 M HCl, we would have $[\text{HCl}] = 0$, $[\text{H}_3\text{O}^+] = [\text{Cl}^-] = 0.10 \text{ M}$.

In similar fashion, a strong base dissociates completely on dissolving in water. Most strong bases are ionic hydroxide compounds, with the general formula $\text{M}(\text{OH})_n$, where $n = 1, 2, 3$, depending on the charge on the cation, M^{n+} . The number of moles per liter of ionic base used to make the solution, the analytical concentration, can be designated $C_{\text{M}(\text{OH})_n}$. Analogous to the strong acid case, for solutions of pure strong base at moderate analytical concentration ($C_{\text{M}(\text{OH})_n} \gg 10^{-7} \text{ M}$), we can generally assume that the base's dissociation supplies virtually all the OH^- ion in the solution; i.e., water's contribution is insignificant. For a given analytical concentration of a pure strong base at moderate concentration, we would have the following values initially and after dissociation:

	$\text{M}(\text{OH})_n(aq) \rightarrow \text{M}^{n+}(aq) + n \text{OH}^-(aq)$		
Initial	$C_{\text{M}(\text{OH})_n}$	0	~ 0
After dissociation	~ 0	$C_{\text{M}(\text{OH})_n}$	$n C_{\text{M}(\text{OH})_n}$

In other words, the concentration of hydroxide ion and cation in the solution are equivalent to the number of moles per liter of base used to make the solution, factoring in the stoichiometry of the dissociation; i.e., $[\text{OH}^-] = n C_{\text{M}(\text{OH})_n}$, $[\text{M}^{n+}] = C_{\text{M}(\text{OH})_n}$. Because of complete dissociation, $[\text{M}(\text{OH})_n] = 0$.

For any acid solution, once $[\text{H}_3\text{O}^+]$ is determined, $[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+]$. Likewise, for any base solution, once $[\text{OH}^-]$ is determined, $[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-]$.

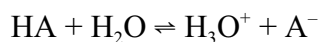
Key Questions

6. Determine the concentrations of H_3O^+ and OH^- in the following solutions of strong acids or bases in water. [Caution: Think about how the acid or base dissociates in water.]

Solution	$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$
$2.5 \times 10^{-3} \text{ M HCl}$		
0.0010 M NaOH		
$7.5 \times 10^{-5} \text{ M Ca(OH)}_2$		

Information (Weak Acid Equilibria)

All acids in water have an acid hydrolysis equilibrium that produces hydronium ion and the conjugate base of the acid:

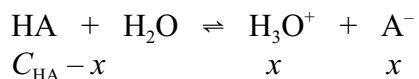


With strong acids this equilibrium lies completely to the right. With weak acids, the equilibrium lies to the left, which means that undissociated acid, HA, is usually the principal species in the solution, with only relatively small concentrations of H_3O^+ and A^- produced from the hydrolysis reaction. The equilibrium constant for the hydrolysis of an acid is labeled K_a , defined as

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

K_a is a constant for a given acid at a particular temperature regardless of the number of moles per liter of acid that was dissolved (the *analytical concentration* of the acid) to make the solution.

We can use K_a to calculate the equilibrium concentrations of all species involved in the hydrolysis reaction (undissociated acid, hydronium ion, and conjugate base) in a solution of a pure weak acid in water. We will only deal with solutions at moderate concentrations, in which we can assume that the added acid is the principal source of hydronium ion. Therefore, we will assume that prior to adding acid we have $[\text{H}_3\text{O}^+] \approx 0$. To set up the problem, let x be the concentration of hydronium ion, $[\text{H}_3\text{O}^+]$, produced by the acid's hydrolysis once equilibrium is established. Then, for an initial concentration of acid HA, symbolized here as C_{HA} , at equilibrium we have



If we substitute these algebraic expressions into K_a , we have

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{C_{\text{HA}} - x}$$

This gives the quadratic equation,

$$x^2 + K_a x - K_a C_{\text{HA}} = 0$$

where $a = 1$, $b = K_a$, and $c = -K_a C_{\text{HA}}$. Ignoring the negative root, we obtain $x = [\text{H}_3\text{O}^+] = [\text{A}^-]$.

When the acid is very weak (very small K_a value) or its analytical concentration is relatively large ($C_{\text{HA}} \gg K_a$), the amount of dissociation of molecular HA may be very small. In this case, we can often ignore x in the expression $[\text{HA}] = C_{\text{HA}} - x$, which means $[\text{HA}] \approx C_{\text{HA}}$. Then, $K_a = x^2/C_{\text{HA}}$, and $x = \sqrt{K_a C_{\text{HA}}} = [\text{H}_3\text{O}^+] = [\text{A}^-]$. As a practical matter, because it takes so little time to calculate, try using $x = \sqrt{K_a C_{\text{HA}}}$, and then calculate the percent dissociation as

$$\% \text{ dissociation} = [\text{H}_3\text{O}^+]/C_{\text{HA}} \times 100\%$$

If this calculation is greater than 5%, go back and use the more exact expression $[\text{HA}] = C_{\text{HA}} - x$, which means you must solve the quadratic equation. Usually, if $C_{\text{HA}} \gg K_a$ by two powers of 10 or more, the acid is probably not appreciably dissociated and you can use $[\text{H}_3\text{O}^+] = \sqrt{K_a C_{\text{HA}}}$. But be sure to check your method by calculating the percent dissociation. If $C_{\text{HA}} \approx K_a$ (within two powers of 10), you will probably have to solve the quadratic equation. By either method, once $[\text{H}_3\text{O}^+]$ has been calculated, the concentration of hydroxide ion in the solution can be determined by solving the K_w expression; i.e., $[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = 1.00 \times 10^{-14}/[\text{H}_3\text{O}^+]$.

Key Questions

7. A 0.0100 M solution of a weak acid HA has a pH of 2.60. What is the value of K_a for the acid? [Hint: What is the actual concentration of undissociated HA, $[\text{HA}]$, in this solution?]
8. What is the pH of 4.0×10^{-2} M benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H} = \text{HBz}$), for which $K_a = 6.46 \times 10^{-5}$? Is it necessary to solve the quadratic equation in this case?
9. Find the concentrations of all species and pH for a 1.0×10^{-3} M HF solution. $K_a = 6.7 \times 10^{-4}$. You will need to find values for $[\text{HF}]$, $[\text{H}_3\text{O}^+]$, $[\text{F}^-]$, and $[\text{OH}^-]$.