LESSON ASSIGNMENT SHEET

LESSON 5 --Conversion of Concentration Units.

TEXT ASSIGNMENT --Paragraphs 5-1 through 5-4.

LESSON OBJECTIVES --After completing this lesson, you should be able to:

5-1. Compute conversions from mol/L to g/dL and from g/dL to mol/L.

5-2. Compute conversions from Eq/L to g/dL and from g/dL to Eq/L.

5-3. Compute conversions from mol/L to Eq/L and from Eq/L to mol/L.

SUGGESTION --After completing the assignment, complete the exercises of this lesson. These exercises will help you to achieve the lesson objectives.

LESSON 5

CONVERSION OF CONCENTRATION UNITS

5-1. DISCUSSION

At times, units of concentration will be given, but another unit of concentration will be required to perform calculations. In this section, we will discuss methods for conversion from one unit of concentration to another.

5-2. CONVERSION FROM mol/L TO g/dL AND FROM g/dL TO mol/L

Before discussing the methods for converting the above units, let's review the definition for each unit.

EQUIVALENT WAYS OF EXPRESSING CONCENTRATION (NO NUMERICAL CONVERSION NECESSARY)

g/dL	=	parts of solute per 100 parts
g/L	=	parts of solute per 1000 parts
molarity	=	moles per liter

The g/dL concentration is defined as parts of solute per 100 parts total solution. The molarity of a solution is defined as the number of moles per liter of solution (mol/L).

CONVERSIONS

	CONCENTRATION EXPRESSED IN	BY	IN UNITS	TO GET CONCENTRATION EXPRESSED IN
Multiply	mol/L	GMW	g/mol	g/L or parts solute per 1000 parts
Multiply	g/dL	10	dL/L	g/L or parts solute per 1000 parts
Multiply	g/dL	$\frac{10}{GMW}$	$\frac{dL}{L} \cdot \frac{mol}{g}$	mol/L

First, let us consider the mol/L concentration. Note that mol/L times the gram molecular weight (g/mol) yields g/L (mol/L x g/mol = g/L). Thus, g/L can also be referred to as parts solute per 1000 parts total solution. And the g/dL concentration times 10 dL/1 L yields parts per 1000. Equivalently, the g/dL concentration times 10 equals the molar concentration times the gram molecular weight. An expression that relates g/dL concentration to mol/L is as follows:

$$(g/dL)\ (10\ dL/1\ L) = (mol/L)(g/mol)$$

a. **Example.** What is the molarity of a 4.0 g/dL NaCl solution?

Solution. Read the problem carefully and determine which formula generates the desired unit.

$$(g/dl)(10\ dL/1\ L) = (mol/L)\ (g/mol)$$

Calculate the GMW of the compound.

NaCl

$$\begin{array}{ll} Na & 23.0 \\ Cl & \underline{+\ 35.5} \\ & 58.5\ g/mol \end{array}$$

Substitute the given information into the formula.

$$(4.0\ g/dL)\ (10\ dL/1\ L) = (mol/L)\ (58.5\ g/mol)$$

Solve for the unknown quantity.

$$\frac{(4.0\ g/dL)(10\ dL/1\ L)}{58.5\ g/mol} = mol/L$$

$$mol/L = \underline{0.68\ mol/L}$$

Using **dimensional analysis:** Read the problem carefully and determine the desired unit of concentration.

Molarity (mol/L)

Knowing the grams per mole for NaCl, use it as an appropriate factor along with the conversion factor that will convert deciliters to liters.

$$\frac{4.0\ g}{dL} \times \frac{1\ mol}{58.5\ g} \times \frac{10\ dL}{1\ L} = 0.68\ mol/L$$

b. **Example.** You are directed to prepare 500 ml of a 5.0 mol/L $FeSO_4$ solution. What is the % concentration of the solution?

Solution. Read the problem carefully and determine which formula generates the desired quantity.

$$(g/dL)(10\ dL/1\ L) = (mol/L)(g/mol)$$

Calculate the GMW of the compound.

$FeSO_4$

Fe	55.8 x 1 =	55.8
S	32.1 x 1 =	32.1
O	16.0 x 4 =	+ 64.0
		151.9 g/mol

Substitute the given information into the formula.

$$(g/dL)(10\ dL/1\ L) = (5.0\ mol/L)(151.9\ g/mol)$$

$$g/dL = \frac{(5.0\ mol/L)(151.9\ g/mol)}{(10\ dL/1\ L)}$$

$$g/dL = \underline{76\ g/dl \text{ or equivalently, } 76\%\ (w/v)}$$

Using **dimensional analysis**: Read the problem carefully and determine the desired unit of concentration.

Percent concentration (%)

The given volume is a distracter. It is not needed to solve this problem.

Use the GMW and an appropriate volume conversion factor to express the concentration in g/dL.

$$\frac{5.0\ mol}{L} \times \frac{151.9\ g}{mol} \times \frac{1\ L}{10\ dL} = 76\ g/dL$$

5-3. CONVERSION FROM Eq/L TO g/dL AND FROM g/dL TO Eq/L

In solving this type of conversion problem, the formula is similar to the one used to solve for mol/L to g/dL. The g/dL concentration is, as previously stated, defined as parts of solute per 100 parts of total solution. The normality of a solution is defined as the number of equivalents per liter of solution (Eq/L). In considering the Eq/L concentration, we note that Eq/L times the gram equivalent weight (g/Eq) yields g/L (Eq/L x g/Eq = g/L). In order to express the g/dL concentration in terms of g/L you must multiply the g/dL concentration times the conversion factor 10 dL/1 L. The formula is comparable to the one used previously. Equivalently, the gram per deciliter concentration times ten equals the Eq/L concentration times the gram equivalent weight. An expression that relates g/dL concentration to Eq/L is as follows:

$$\mathbf{(g/dL)(10\ dL/1\ L) = (Eq/L)(g/Eq)}$$

a. **Example.** What is the g/dL concentration of a 1.5 Eq/L NaOH solution?

Solution. Read the problem carefully and determine which formula generates the desired quantity.

$$(g/dL)(10\ dL/1\ L) = (Eq/L)(g/Eq)$$

Determine the GEW of the compound.

NaOH

$$\begin{array}{ll} Na & 23.0 \\ O & 16.0 \\ H & \underline{+\ 1.0} \\ & 40.0\ g/mol \end{array}$$

$$\frac{40.0\ g/mol}{1\ Eq/mol} = 40.0\ g/Eq$$

Substitute the given information and solve for the unknown quantity.

$$(g/dL)(10\ dL/1\ L) = (1.5\ Eq/L)(40.0\ g/Eq)$$

$$g/dL = \frac{(1.5\ Eq/L)(40.0\ g/Eq)}{10\ dL/1\ L}$$

$$g/dL = \underline{6.0\ g/dL}$$

Using **dimensional analysis**: Read the problem carefully and determine the desired unit of concentration.

Percent concentration (g/dL)

Use the GEW and the appropriate volume conversion factor to express the concentration as g/dL.

$$\frac{1.5\ Eq}{L} \times \frac{40.0\ g}{Eq} \times \frac{1\ L}{10\ dL} = 6.0\ g/dL$$

b. **Example.** What is the Eq/L concentration of a 5.0 g/dL $CaCO_3$ solution?

Solution. Read the problem carefully and determine which formula generates the desired quantity.

$$(g/dL)(10\ dL/1\ L) = (Eq/L)(g/Eq)$$

Determine the GEW of the compound.

$CaCO_3$

Ca	40.1 x 1	=	40.1
C	12.0 x 1	=	12.0
O	16.0 x 3	=	+ 48.0
			100.1 g/mol

$$\frac{100.1 \text{ g/mol}}{2 \text{ Eq/mol}} = 50.05 \text{ g/Eq}$$

Substitute the given information and solve for the unknown quantity.

$$(5.0 \text{ g/dL})(10 \text{ dL/1 L}) = (\text{Eq/L})(50.05 \text{ g/Eq})$$

$$\text{Eq/L} = \frac{(5.0 \text{ g/dL})(10 \text{ dL/1 L})}{50.05 \text{ g/Eq}}$$

$$\text{Eq/L} = \underline{1.0 \text{ Eq/L}}$$

Using **dimensional analysis:** Read the problem carefully and determine the desired unit of concentration.

Normality (Eq/L)

Determine the GEW of the compound.

$$\frac{100.1 \text{ g}}{\text{mol}} \times \frac{1 \text{ mol}}{2 \text{ Eq}} = 50.05 \text{ g/Eq}$$

Use the GEW and the appropriate volume conversion factor to express the Eq/L concentration.

$$\frac{5.0 \text{ g}}{\text{dL}} \times \frac{1 \text{ Eq}}{50.05 \text{ g}} \times \frac{10 \text{ dL}}{1 \text{ L}} = 1.0 \text{ Eq/L}$$

5-4. CONVERTING FROM mol/L TO Eq/L AND FROM Eq/L TO mol/L

The major difference between mol/L and Eq/L is the use of molecular weight when determining mol/L and the use of the equivalent weight when determining Eq/L. Since the gram equivalent weight is calculated by dividing the gram molecular weight by the equivalents per mole (Eq/mol = TPIV), the conversion will be based on the use of Eq/mol expression (TPIV).

a. Formulas.

(1) $\text{mol/L} = \dfrac{\text{Eq/L}}{\text{Eq/mol}}$ **(2)** $\text{Eq/L} = (\text{mol/L})(\text{Eq/mol})$

b. **Example.** What is the mol/L concentration of a 4 Eq/L $Ba(OH)_2$ solution?

Solution. Read the problem carefully and determine which formula generates the desired unit.

$$\text{mol/L} = \frac{\text{Eq/L}}{\text{Eq/mol}}$$

By inspection (TPIV) we see that there are 2 Eq/mol

Substitute the given information and solve the unknown quantity.

$$\text{mol/L} = \frac{4\ \text{Eq/L}}{2\ \text{Eq/mol}}$$

$$\text{mol/L} = \underline{2\ \text{mol/L}}$$

Using **dimensional analysis:** Read the problem carefully and determine the desired unit of concentration.

Molarity (mol/L)

Determine, as above, the number of equivalents per mole of compound and use it as an appropriate factor to express the solution in the desired units.

$$\frac{4.0\ \text{Eq}}{\text{L}} \times \frac{1\ \text{mol}}{2\ \text{Eq}} = 2.0\ \text{mol/L}$$

c. **Example.** What is the Eq/L concentration of a 1 mol/L $AlPO_4$ solution?

Solution. Read the problem carefully and determine which formula generates the desired unit.

$$\text{Eq/L} = (\text{mol/L})(\text{Eq/mol})$$

Substitute the given information and solve for the unknown quantity.

$$\text{Eq/L} = (1\ \text{mol/L})(3\ \text{Eq/mol})$$

$$\text{Eq/L} = \underline{3\ \text{Eq/L}}$$

Using **dimensional analysis:** Read the problem carefully and determine the desired unit of concentration.

Normality (Eq/L)

Determine the number of equivalents per mole of compound and use the appropriate conversion factor to express the solution in the desired units.

$$\frac{1\ \text{mol}}{\text{L}} \times \frac{3\ \text{Eq}}{1\ \text{mol}} = 3\ \text{Eq/L}$$

EXERCISES, LESSON 5

REQUIREMENT. The following exercises are to be answered by writing the answer in the space provided at the end of the question.

After you have completed all the exercises, turn to "Solutions to Exercises," at the end of the lesson and check your answers with the review solutions.

1. Find the Eq/L concentration of a 4.0 mol/L $Fe_2(SO_4)_3$ solution.

____

2. What is the g/dL concentration of a 2.0 Eq/L NH_4NO_3 solution?

____

3. Calculate the mEq/L concentration of a 0.10 g/dL Na_2SO_4 solution.

____

4. A 1-liter flask contains 500 mL of a 0.75 Eq/L $CuWO_4$ solution. Calculate the mol/L concentration of the $CuWO_4$ solution.

____

5. Determine the mol/L concentration of a 20 g/dL $CaCO_3$ solution.

____

6. A $NaNO_3$ solution has a 300 mg/dL concentration. What is the mol/L concentration of the solution?

____

7. What is the Eq/L concentration of 100 mL of a 2.0 mol/L H_2SO_4?

____

8. Find the mg/dL concentration of a 800 mEq/L $(NH_4)_2SO_4$ solution.

____

9. What is the mol/L concentration of a 200 mEq/L $Cu_2CO_3 \cdot 5HOH$ solution?

____

10. What is the Eq/L concentration of a 745 mg/dL KCl solution?

____

SOLUTIONS TO EXERCISES, LESSON 5

1. 24 Eq/L (para 5-4)
2. 16 g/dL (para 5-3)
3. 14.1 mEq/L (para 5-3)
4. 0.38 mol/L (para 5-4)
5. 2.0 mol/L (para 5-2)
6. 0.0353 mol/L (para 5-2)
7. 4.0 Eq/L (para 5-4)
8. 5280 mg/dL (para 5-3)
9. 0.100 mol/L (para 5-4)
10. 0.0999 Eq/L (para 5-3)

LESSON ASSIGNMENT SHEET

LESSON 6 --pH and Buffers.

LESSON ASSIGNMENT --Paragraphs 6-1 through 6-23. You are still responsible for materials in the previous lessons.

LESSON OBJECTIVES --After completing this lesson, you should be able to:

6-1. Given the molar concentration of an acid or base, compute the pH and pOH.

6-2. Solve buffers problems and perform related computations.

SUGGESTION --After completing the assignment, complete the exercises of this lesson. These exercises will help you to achieve the lesson objectives.

LESSON 6

pH and BUFFERS

Section I. INTRODUCTION

6-1. DISCUSSION

a. The interaction of charged particles in which the total number of protons do not equal the number of electrons is responsible for many chemical reactions. These charged particles are called **ions**. A **cation** is an ion in which the protons are more numerous than the electrons (+ charge), and anions are ions in which the electrons outnumber the protons (- charge). These oppositely charged ions are attracted to each other and form bonds called **ionic bonds**. When ionically bound compounds are dissolved in a solvent, the ions separate. This separation is known as **dissociation** or **ionization**. The only way in which most ions can undergo chemical reaction is to be in this dissociated state.

b. Three general types of ionic compounds exist: acids, bases, and salts. Simply and incompletely stated, **acids** are compounds that contribute hydrogen ions to a solution, **bases** are compounds that contribute hydroxide ions to the solution, and salts may yield neither hydrogen nor hydroxide ions to the solution. The concentration of the hydrogen and hydroxide ions will determine the degree of acidity or alkalinity of a solution, and thus have an effect on the kinds of reactions and the speed of the reactions that will occur. It is important, therefore, to know the relative concentrations of the hydrogen and hydroxide ions in a solution.

c. Before discussing hydrogen and hydroxide ion concentration further, it will be important to consider in greater detail the definition of an acid and a base. There are several definitions of the terms acid and base. We will examine two of the definitions that will aid you in further course work.

6-2. ARRHENIUS CONCEPT

An **acid** is a substance that will produce hydrogen ions (H^+) in an aqueous solution, and a **base** is a substance that will produce hydroxide ion (OH^-) in an aqueous solution. It is important to note that hydrogen ions do not exist as such in an aqueous solution. Each hydrogen ion is associated with one molecule of water to produce a hydronium ion, H_3O^+.

$$H^+ + H_2O \Longleftrightarrow H_3O^+$$

When hydrochloric acid (HCl), which exists in its pure state as a gas, is dissolved in water, the following reaction takes place:

$$HCl + H_2O \Longleftrightarrow H_3O^+ + Cl^-$$

The hydronium ion can easily react with other groups as a proton donor. The hydrogen ion itself is made up of one proton.

<u>NOTE</u>: The terms hydronium ion, hydrogen ion, and proton donor may be used interchangeably. However, we will simply refer to the hydrogen ion in future course work, but you should understand that this actually implies the presence of the hydronium ion.

One of the primary drawbacks of the Arrhenius concept is that it defines only aqueous solutions as acids and bases. Other theories allow for nonaqueous solutions.

a. **Examples of Arrhenius Acids.**

(1) HCl - hydrochloric acid.

(2) H_2SO_4 - sulfuric acid.

(3) H_3PO_4 - phosphoric acid.

b. **Examples of Arrhenius Bases.**

(1) NaOH - sodium hydroxide.

(2) $Ca(OH)_2$ - calcium hydroxide.

(3) KOH - potassium hydroxide.

6-3. BRØNSTED-LOWRY THEORY

The Brønsted-Lowry theory presents a broader definition of the terms acid and base. An acid is a proton donor and a base is a proton acceptor. HCl in solution is a Brønsted-Lowry acid not only because it forms hydrogen ions but because it is able to give up that hydrogen ion to another substance, such as to a molecule of water to form hydronium ions. For HCl, the difference between the two definitions seems minor. However, it becomes important when the solvent is not water. For example, when HCl reacts with NH_3 (ammonia), the proton is given up by the HCl and accepted by the NH_3, making the HCl an acid and NH_3 a base.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NH_3} \Longleftrightarrow \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{Cl^-}$$

a. **Examples of Brønsted-Lowry Acids.**

(1) NH_4^+ - ammonium ion.

(2) $HC_2H_3O_2$ - acetic acid.

(3) H_2CO_3 - carbonic acid.

b. **Examples of Brønsted-Lowry Bases.**

(1) Cl^- - chloride ion.

(2) NH_3 - ammonia.

(3) $Fe(OH)_2$ - iron (II) hydroxide.

6-4. WEAK ACIDS/BASES VERSUS STRONG ACIDS/BASES

As discussed previously, we stated that acids, bases, and salts are ionic compounds. Substances that break up into ions in solution are termed **electrolytes** because the solution has the ability to conduct electrical current. A **strong electrolyte** (acid or base) is a substance that exhibits a high degree of ionization, and a **weak electrolyte** is a substance that only partially ionizes.

a. Hydrochloric (HCl), sulfuric (H_2SO_4), and nitric (HNO_3) acids are strong acids because they exhibit a high degree of ionization in aqueous solutions. Hydrobromic (HBr), hydroiodic (HI), and perchloric ($HClO_4$) acids are also considered strong acids. All others are weak.

b. The alkaline metal (Group IA i.e., lithium, sodium, potassium,...) hydroxides and the alkaline earth (Group IIA i.e., magnesium, calcium, strontium,...) hydroxides are strong bases. Other bases are weak ones.

c. Hydrogen and hydroxide only affect pH or pOH when in the ionized form.

Section II. DYNAMIC EQUILIBRIUM

6-5. DISCUSSION

When an acid ionizes, an equilibrium is established between the un-ionized acid and its ions. This is indicated by double arrows or a doubled-headed arrow in an equation, showing that the two reactions occur simultaneously. HA is used to represent any acid made up of hydrogen and some anion.

$$HA \Longleftrightarrow H^+ + A^-$$

At the same time, the acid molecule is dissociating, a certain percentage of the ions are reassociating to reform the acid. When the acid is first placed in water, a high degree of dissociation occurs, and the rate of the forward reaction is greater. Gradually, as more ions are formed, the rate of the reverse reaction increases. Eventually, a state of equilibrium is reached in which molecules are being ionized and reassociated at a given rate. Equilibrium exists when the rates, not the number of molecules or concentrations, of the opposing reactions are equal. This is a dynamic, constant process and continues until a force is added to change this equilibrium. For example, if the temperature is increased, the rates of the reaction are increased, and a new equilibrium state is reached. Removing one of the ions or tying them up with another reaction will also shift the equilibrium.

6-6. LAW OF MASS ACTION

a. **Law.** The law of mass action states that the rate of reaction is proportional to the product of the molar concentrations of the reactants.

$$A + B \rightleftharpoons C + D$$

For this reaction, A and B are the reactants, and C and D are the products. The rate at which C and D are formed is proportional to the concentration of A and B.

$$\text{rate} = K_1 [A] [B]$$

where K_1 is a proportionality constant, and the brackets denote mol/L concentration of the enclosed substance.

The rate for the reverse reaction is:

$$\text{rate} = K_2 [C] [D]$$

b. **Equilibrium Constant (K_{eq}).**

The constants K_1 and K_2 are different. The ratio of the constants is known as the equilibrium constant (K_{eq}), dissociation constant, or ionization constant.

$$K_{eq} = \frac{K_1}{K_2}$$

(1) At equilibrium, the rates of the forward and reverse reactions are equal.

$$\text{rate}_f = \text{rate}_r$$

$$\text{rate}_f = K_1 [A] [B]$$

$$\text{rate}_r = K_2 [C] [D]$$

$$K_1 [A] [B] = K_2 [C] [D]$$

$$\frac{K_1}{K_2} = \frac{[C] [D]}{[A] [B]}$$

$$\frac{K_1}{K_2} = K_{eq}$$

(2) Simply, the ionization (equilibrium) constant is equal to the product of the mol/L concentrations of the products formed in the reaction divided by the product of the concentrations of the reactants.

(3) The equilibrium constant for an acid is called the K_a and for a base the K_b.

(4) K_a and K_b are determined for weak acids and bases only. If the K_a or K_b of a strong acid or base, respectively, were determined it would be an infinitely large number.

(5) Values of equilibrium constants are interpreted as follows:

(a) The constant indicates the strength of a weak electrolyte.

(b) The smaller the value of the K_a or K_b, the weaker the acid or base respectively.

6-7. EXAMPLE

What is the $[H^+]$ of a 0.100 mol/L solution of acetic acid if the K_a for $HC_2H_3O_2$ is 1.75×10^{-5}?

Solution. Determine the equation for the dissociation of the weak acid.

$$HC_2H_3O_2 \Longleftrightarrow H^+ + C_2H_3O_2^-$$

Write the equilibrium expression.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Substitute the given information, and solve for the unknown quantity.

$$1.75 \times 10^{-5} \text{ mol/L} = \frac{[H^+]\ [C_2H_3O_2^-]}{0.100 \text{ mol/L}}$$

<u>NOTE</u>: Although the actual concentration of the acetic acid is less than 0.100 mol/L after ionization, it is a negligible amount (less than 5%). In your future course work, the amount of ionized acid or base in this type of problem should be considered to be a negligible amount.

Substitute the variable x for H^+ and $C_2H_3O_2^-$ since for every dissociated molecule of $HC_2H_3O_2$, one hydrogen ion and one acetate radical are produced.

$$x^2 = (1.75 \times 10^{-5} \text{ mol/L})\ (0.100 \text{ mol/L}) = 1.75 \times 10^{-6} \text{ mol}^2/\text{L}^2$$

$$x = [H^+] = \underline{1.32 \times 10^{-3}} \text{ mol/L}$$

<u>NOTE</u>: By convention, the equilibrium constants of weak electrolytes are written without units. However, they do have units.

Section III. DISSOCIATION OF WATER

6-8. DISCUSSION

Although water is not an electrolyte, its molecules do have a limited tendency to dissociate into H^+ and OH^- ions.

$$HOH \rightleftharpoons H^+ + OH^-$$

It can be shown that the tendency of water to dissociate is given by:

$$K = \frac{[H^+]\,[OH^-]}{[HOH]}$$

At 25°C, the value of K is 1.8×10^{-16}.

6-9. ION PRODUCT OF WATER

a. Since undissociated water is present in great excess, its concentration is virtually constant at 55.6 mol/L.

NOTE: The gram molecular weight of water is 18.0; therefore, in 1.00 L (approximately 1000 grams), there are:

$$\frac{\dfrac{(1000\ g)}{(18.0\ g/mol)}}{1\ L} = 55.6\ mol/L$$

b. This constant value for the concentration of water can be incorporated into the dissociation constant to give a new constant, the ion product of water, or K_w.

$$1.8 \times 10^{-16} = \frac{[H^+]\,[OH^-]}{[55.6]}$$

$$[H^+]\,[OH^-] = 1.0 \times 10^{-14}$$

Therefore, in pure water,

$$[H^+] = 1.0 \times 10^{-7}\ mol/L$$

$$[HO^-] = 1.0 \times 10^{-7}\ mol/L$$

$$K_w = [H^+]\,[HO^-] = 1.0 \times 10^{-14}$$

c. It is important to realize that the ion product of water, $[H^+]$ $[OH^-]$, is constant for all aqueous solutions, even those that contain dissolved acids or bases.

(1) If a large number of H^+ ions are added to pure water, the concentration of OH^- ions must decrease in order that the product of $[H^+]$ $[OH^-]$ remains the same.

(2) Conversely, if a large number of hydroxyl ions are added, the $[H^+]$ will have to decrease.

Section IV. pH and pOH

6-10. CONCEPT OF pH

Pure water contains an equal concentration of hydrogen and hydroxide ion. Thus, it is a neutral substance, neither acidic nor basic. If a solution has an excess of hydrogen ions, the solution will be acidic. If a solution has an excess of hydroxide ions, the solution will be alkaline. It is customary to use the hydrogen ion concentration (pH) as a measure of the acidity or alkalinity of a solution. pH is a unit of concentration that allows the technician to work with very dilute concentrations of hydrogen and hydroxide ion in a convenient form. This scale permits the representation of the enormous range of the possible $[H^+]$ concentrations from a 1.0 mol/L $[H^+]$ to a 1.0×10^{-14} mol/L $[H^+]$.

6-11. APPLICATION OF CONCEPT OF pH

The notation p relates to "negative log of." Logarithms are discussed in lesson 1, and there is a four-place logarithm table in Appendix B. pH is mathematically defined as:

$$-\log [H^+] \text{ or } \log 1/[H^+]$$

a. **Example 1.** What is the pH of a 0.133 mol/L HCl solution?

Solution. Select the expression that allows you to solve for the unknown quantity.

$$pH = -\log [H^+]$$

Substitute the given information, and solve for the unknown quantity.

$$pH = -\log 0.133 = -\log [1.33 \times 10^{-1}] = -(0.1239 - 1)$$

$$pH = -(-0.876)$$

$$pH = \underline{0.876}$$

b. **Example 2.** What is the pH of a 0.020 mol/L acid solution that is ionized 1.8%?

Solution. From previous discussion, hydrogen or hydroxide do not contribute to the acidity or alkalinity of a solution unless ionized. So in this problem consider only that hydrogen ion that is ionized.

$$pH = -\log [H^+]$$

$$pH = -\log [(0.020 \text{ mol/L}) (0.018)] = -\log [3.6 \times 10^{-4}] = -(.5563 - 4)$$

$$pH = \underline{3.4}$$

c. **Example 3.** Determine the pH of a 0.0100 mol/L $HC_2H_3O_2$ solution. The K_a of the acid is 1.75×10^{-5}.

Solution. In determining the pH of a solution of weak electrolyte, you must first calculate the hydrogen ion concentration. Acetic acid ionizes as follows:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Write the equilibrium expression:

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Substitute the given information, and solve for the hydrogen ion concentration.

$$1.75 \times 10^{-5} \text{ mol/L} = \frac{[H^+]\ [C_2H_3O_2^-]}{0.100 \text{ mol/L}}$$

Substitute the variable x for H^+ and $C_2H_3O_2^-$, since one hydrogen ion and one acetate ion are produced for every dissociated molecule of $HC_2H_3O_2$.

$$[H^+]\ [C_2H_3O_2^-] = (1.75 \times 10^{-5})\ (0.0100 \text{ mol/L})$$

$$x^2 = (1.75 \times 10^{-5} \text{ mol/L})\ (0.0100 \text{ mol/L})$$

$$x^2 = 1.75 \times 10^{-7} \text{ mol}^2/\text{L}^2$$

$$x = [H^+] = 4.18 \times 10^{-4} \text{ mol/L}$$

Using the calculated value for the hydrogen ion concentration, determine the pH of the solution.

$$pH = -\log [H^+]$$

$$pH = -\log [4.18 \times 10^{-4} \text{ mol/L}] = -\ (.6212 - 4)$$

$$pH = -(-3.38)$$

$$pH = \underline{3.38}$$

6-12. **pOH**

pOH is mathematically defined as:

$$-\log [OH^-] \text{ or } \log 1/[OH^-]$$

<u>NOTE</u>: pH and pOH have no unit of report.

6-13. **pH SCALE**

a. pH range: 0-14

b. Neutral: pH 7

c. Acidic: less than pH 7

d. Basic: greater than pH 7

pH below 7	pH = 7	pH above 7
0		14
More Acidic	Neutral	More Basic

In examining the definition of pH, we find that there is an inverse relationship between hydrogen ion concentration and pH. As $[H^+]$ increases, pH decreases and vice versa. Also, notice that each increase of one unit on the pH scale corresponds to a tenfold decrease in $[H^+]$, and each decrease of one unit on the pH scale corresponds to a tenfold increase in $[H^+]$. If this is true, then as the $[H^+]$ increases, $[HO^-]$ decreases, and as $[H^+]$ decreases, $[OH^-]$ increases.

6-14. **pOH SCALE**

a. pOH range: 0 -14

b. Neutral: pOH 7

c. Acidic: greater than pOH 7

d. Basic: less than pOH 7

pOH below 7	pOH = 7	pOH above 7
0		14
More Basic	Neutral	More Acidic

Section VI. BUFFERS

6-20. DISCUSSION

Buffer systems are commonly used in the laboratory to help maintain a constant pH in a reaction mixture. A buffer solution acts to resist a change in pH. A buffer is composed of either a weak acid and its salt or a weak base and its salt. Buffers made up of a weak acid and its salt are called acidic buffers and function from pH 0 to 7. Basic buffers consist of a weak base and its salt and function from pH 7 to 14.

6-21. MECHANISM OF ACTION

a. **Addition of a Strong Acid.** A common buffer used in the laboratory is the acetic acid/acetate buffer. As acid is added $[H^+]$ into the solution, it will react with the acetate anion from the salt (proton acceptor) forming acetic acid. Since acid is added, a shift in the equilibrium of the solution will occur, but the amount of free hydrogen ions in solution will be controlled by the ionization constant of the acetic acid formed and only a slight change in $[H^+]$ takes place.

Buffer system:

$HC_2H_3O_2/NaC_2H_3O_2$ (Acetic acid/sodium acetate)

Buffer system with HCl added:

$$H^+ + Cl^- + Na^+ + C_2H_3O_2^- \Longleftrightarrow HC_2H_3O_2 + Cl^- + Na^+$$

b. **Addition of a Strong Base.** As base is added to this buffer, acetic acid reacts with the base to form salt (acetate ions) and water. Once again a shift in the equilibrium of the solution occurs but with a minimal change in pH.

NaOH added:

$$Na^+ + OH^- + HC_2H_3O_2 \Longleftrightarrow Na^+ + C_2H_3O_2^- + H_2O$$

c. **Notes.**

(1) A buffer's ability to resist changes in pH is limited to the concentration of either the weak acid of base and its salt. The addition of an excessive amount of either acid or base will "exhaust" the buffering capacity of the buffer.

(2) The closer the pH of the buffer to the pK_a or pK_b of the weak acid or base respectively the greater the buffering capacity.

6-22. THE HENDERSON-HASSELBALCH EQUATION

The preparation of laboratory buffers can be accomplished by using the Henderson-Hasselbalch equation. The equation is derived from the ionization constant of weak acids and bases.

$$K = \frac{[H^+]\,[A^-]}{[HA]}$$

The hydrogen ion concentration can be calculated by rearranging the equation.

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

Because $[H^+]$ is usually expressed as pH, it is usually more convenient to express all concentration in this equation in logarithmic form.

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

Since pH = $-\log\,[H^+]$ multiply both sides of the equation by -1.

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

Restated:

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

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

The expression relating pOH to the components of a buffer may be developed similarly.

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

6-23. SOLVING BUFFER PROBLEMS

The most important consideration when preparing a buffer is determining whether an acidic or basic buffer is being prepared. Examine the components of the buffer. If a weak acid and its salt are the components, use the expression for acidic buffers. If a weak base and its salt are used, select the expression for basic buffers.

a. **Example 1.** Calculate the pH of a buffer solution that contains 0.010 mol/L acetic acid and 0.020 mol/L sodium acetate. The K_a for acetic acid is 1.75×10^{-5}.

Solution. Read the problem carefully, and select the expression that allows you to solve for the unknown quantity.

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

Make any necessary conversions.

$$pK_a = -\log K_a$$

$$pK_a = -\log (1.75 \text{ X } 10^{-5})$$

$$pK_a = 4.76$$

Substitute the given information, and solve for the unknown quantity.

$$pH = 4.76 + \log \frac{0.020 \text{ mol/L}}{0.010 \text{ mol/L}}$$

$$pH = 4.76 + 0.301$$

$$pH = \underline{5.06}$$

b. **Example 2.** What is the pH of a buffer solution that contains 1.50 X 10^{-3} mol/L NH_4Cl and 2.00 X 10^{-4} mol/L NH_4OH? The pK_b for ammonium hydroxide is 4.75.

Solution. Read the problem carefully, and select the expression that allows you to solve for the unknown quantity. Note that you are dealing with a basic buffer from which you must determine pH.

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

Substitute the given information, and solve for the unknown quantity.

$$pOH = 4.75 + \log \frac{1.50 \text{ X } 10^{-3} \text{ mol/L}}{2.00 \text{ X } 10^{-4} \text{ mol/L}}$$

$$pOH = 4.75 + 0.8751$$

$$pOH = 5.63$$

Now that you have determined the pOH, using the appropriate expression, determine the pH of the buffer.

$$14 = pH + pOH$$

$$pH = 14 - pOH$$

$$pH = 14 - 5.63$$

$$pH = \underline{8.37}$$

c. **Example 3.** What amount of salt/acid is required to prepare a 0.100 mol/L acetate buffer at a pH of 5.50? The pK_a of acetic acid is 4.76.

Solution. At times the pK of the acid/base of a buffer and the total concentration of the buffer is known, and the amount of salt and acid/base required to prepare a buffer must be calculated.

After reading the problem carefully, select the expression that allows you to solve for the unknown quantity.

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

Substitute the given information, and solve for the unknown quantity.

$$5.50 = 4.76 + \log \frac{[salt]}{[acid]}$$

$$5.50 - 4.76 = \log \frac{[salt]}{[acid]}$$

$$0.74 = \log \frac{[salt]}{[acid]}$$

$$\text{antilog } 0.74 = \frac{[salt]}{[acid]}$$

$$5.5 = \frac{[salt]}{[acid]} = \frac{5.5 \text{ mol/L}}{1 \text{ mol/L}}$$

You have now established the proper ratio of salt and acid that will yield the desired pH. However, the problem states that a molar concentration of 0.100 mol/L for the buffer is desired. This mol/L concentration is the sum of the mol/L concentrations of the salt and the acid. The mol/L concentration of the buffer, based on your calculations so far, is 6.5 mol/L. The following method is one of several that you may employ to determine the concentrations necessary to yield the proper mol/L concentration of the buffer while maintaining the proper ratio.

Express the desired mol/L concentration of the buffer as an equality.

$$[salt] + [acid] = 0.100 \text{ mol/L}$$

Solve the equality for either [salt] or [acid].

$$[salt] = 0.100 \text{ mol/L} - [acid]$$

Now based on the substitution property, you are able to express the [salt] in terms of [acid], and in effect, derive an equation in one variable instead of the two, in the original expression.

$$5.5 = \frac{[salt]}{[acid]}$$

$$5.5 = \frac{0.100 \text{ mol/L} - [acid]}{[acid]}$$

Simplify the expression by clearing the fraction.

$$5.5\,[acid] = 0.100 \text{ mol/L} - [acid]$$

Solve the expression for [acid].

$$5.5\,[acid] + [acid] = 0.100 \text{ mol/L}$$

$$6.5\,[acid] = 0.100 \text{ mol/L}$$

$$[acid] = \frac{0.100 \text{ mol/L}}{6.5}$$

$$[acid] = \underline{0.0154} \text{ mol/L, or equivalently,}$$

$$\underline{1.54 \times 10^{-2}} \text{ mol/L}$$

To determine the amount of salt required, substitute the calculated value of the acid concentration in the expression relating the salt and acid concentration to the desired mol/L concentration of the buffer.

$$[salt] = 0.100 \text{ mol/L} - [acid]$$

$$[salt] = 0.100 \text{ mol/L} - 0.0154 \text{ mol/L}$$

$$[salt] = 0.0846 \text{ mol/L, or equivalently,}$$

$$8.46 \times 10^{-2} \text{ mol/L}$$

d. **Example 4.** What amount of salt/base is required to prepare a 0.100 mol/L ammonia buffer at a pH of 9.8? The pK_b for ammonium hydroxide is 4.75.

Solution. After reading the problem carefully, note that you are to prepare a basic buffer of a certain pH. Select an expression that will allow you to solve for the unknown quantity.

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

Convert pH to pOH.

$$14 = pH + pOH$$

$$pOH = 14 - pH$$

$$pOH = 14 - 9.8$$

$$pOH = 4.2$$

Substitute the given values, and solve for the unknown quantity.

$$4.2 = 4.75 + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$4.2 - 4.75 = \log \frac{[\text{salt}]}{[\text{base}]}$$

$$-0.6 = \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{antilog } (-0.6) = \frac{[\text{salt}]}{[\text{base}]}$$

$$0.3 = \frac{[\text{salt}]}{[\text{base}]}$$

Express the desired mol/L concentration of the buffer as an equality.

$$[\text{salt}] + [\text{base}] = 0.100 \text{ mol/L}$$

Solve the equality for either [salt] or [base].

$$[\text{salt}] = 0.100 \text{ mol/L} - [\text{base}]$$

Now, based on the substitution property, you are able to express the [salt] in terms of [base], and in effect derive an equation in one variable instead of the two in the original expression.

$$0.3 = \frac{[\text{salt}]}{[\text{base}]}$$

$$0.3 = \frac{0.100 \text{ mol/L} - [\text{base}]}{[\text{base}]}$$

Simplify the expression by clearing the fraction.

$$0.3 \, [\text{base}] = 0.100 \text{ mol/L} - [\text{base}]$$

Solve the expression for [base].

$$0.3 \, [\text{base}] + [\text{base}] = 0.100 \text{ mol/L}$$

$$1.3 \, [\text{base}] = 0.100 \text{ mol/L}$$

$$[\text{base}] = \frac{0.100 \text{ mol/L}}{1.3}$$

$$[\text{base}] = \underline{0.077 \text{ mol/L}}$$

or equivalently, $\underline{7.7 \times 10^{-2}}$ mol/L

To determine the amount of salt required, substitute the calculated value of the base concentration in the expression relating the salt and base concentration to the desired mol/L concentration of the buffer.

$$[\text{salt}] = 0.100 \text{ mol/L} - [\text{base}]$$

$$[\text{salt}] = 0.100 \text{ mol/L} - 0.077 \text{ mol/L}$$

$$[\text{salt}] = \underline{0.023 \text{ mol/L}}$$

or equivalently, $\underline{2.3 \times 10^{-2}}$ mol/L

EXERCISES, LESSON 6

REQUIREMENT. The following exercises are to be answered by writing the answer in the space provided at the end of the question.

After you have completed all the exercises, turn to "Solutions to Exercises," at the end of the lesson, and check your answers with the review solutions.

1. **What is the pH of a 4.00×10^{-4} mol/L HCl solution?**

____

2. **What is the pH of a 0.100 mol/L $HC_2H_3O_2$ that ionizes 1.3%?**

____

3. **What is the pOH of a 0.250 mol/L H_2SO_4 solution? (<u>Note:</u> Use the given concentration for pH and pOH calculations that involve polyprotic acids, that is, acids with more than one hydrogen.)**

____

4. What is the pH of a 1.40 X 10^{-2} mol/L $Ca(OH)_2$ solution? (NOTE: To determine the actual hydroxide concentration of this and like compounds multiply the given concentration by the number of hydroxide ions per molecule.)

____

5. What is the pH of a buffer prepared by adding 1.20 X 10^{-3} mol/L $NaC_2H_3O_2$ and 1.20 X 10^{-2} mol/L $HC_2H_3O_2$? The K_a for acetic acid is 1.75 X 10^{-5}.

____

6. What is the pOH of a buffer prepared by adding 3.50 X 10^{-5} mol/L NH_4OH and 2.50 X 10^{-4} mol/L NH_4Cl? The pK_b for NH_4OH is 4.75.

____

7. What is the pH of the buffer in exercise 6?

____

8. An acetate buffer, pH 5.20, was prepared using 0.100 mol/L acetic acid. The pK_a for acetic acid is 4.76. What concentration of salt is needed?

____

9. A 0.050 mol/L bicarbonate buffer with a pH of 5.60 is to be prepared. The pK_a of carbonic acid is 6.12. What concentration of sodium bicarbonate and carbonic acid are needed to prepare the buffer?

____

10. A 0.0670 mol/L buffer, pH 7.10 is to be prepared. The pK_a of KH_2PO_4 is 4.71. A volume of 1.00 liter is needed.

a. What concentration of KH_2PO_4 and Na_2HPO_4 is required?

____

b. What weight of each constituent is needed to prepare the buffer?

____

11. An ammonia buffer pH 7.60 with a concentration of 1.20×10^{-2} mol/L is required. The K_b for NH_4OH is 1.79×10^{-5}. The desired volume is 500 mL.

a. What concentration of NH_4OH and NH_4Cl are required?

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b. What weight of NH_4Cl is needed?

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c. How many milliliters of NH_4OH with a S.G. 0.950 and percent purity of 28% are required?

SOLUTIONS TO EXERCISES, LESSON 6

1. pH = 3.40 (para 6-11)
2. pH = 2.9 (para 6-11)
3. pOH = 13.7 (para 6-12)
4. pH = 12.4 (para 6-15)
5. pH = 3.76 (para 6-23)
6. pOH = 5.60 (para 6-23)
7. pH = 8.40 (para 6-23)
8. [salt] = 0.275 mol/L (para 6-23)
9. [salt] = 0.012 mol/L
   [acid] = 0.038 mol/L (para 6-23)
10. a. [acid] = 0.000272 mol/L
       [salt] = 0.0667 mol/L (para 6-23)
    b. Acid = 0.0370 g
       Salt = 9.47 g (lesson 3)
11. a. [base] = 0.000261 mol/L
       [salt] = 0.0117 mol/L (para 6-23)
    b. 0.313 g (lesson 3)
    c. 0.0172 mL (para 6-23)