

Concentrations Based on the Volume of Solvent

1. Molarity (M), is the number of moles of solute dissolved in one liter of solution. Molarity is also called molar concentration. The molarity of a solution can be calculated when the number of grams of the substance in the solution, the volume of the solution, and the molecular weight or formula weight of the substance are known. Conversely, the number of grams of the substance needed to prepare a solution of a particular molarity can be calculated if the final volume of the solution is defined and the molecular weight or formula weight of the substance is known. Dilute solutions are named by using the appropriate prefix.

The equation defining molarity is:

$$\text{molarity (M)} \times \text{liters of solution} = \text{moles of solute}$$

The following are true for a solution that is diluted. It's clear, that

$$M \times V = \text{constant}$$

2. Normality (N) is the number of equivalents of a solute dissolved in one liter of solution. For an acid or base, an equivalent is the molecular weight or formula weight of the acid or base expressed in grams divided by the number of moles of hydronium (H_3O^+) or hydroxyl ions produced by this amount of acid or base.

$$\text{equivalents} = \text{moles}/n$$

n = number of hydronium or hydroxyl ions.

The term equivalent weight is used and related to molecular weight and formula weight by

$$\text{equivalent weight} = \text{molecular weight} / n = \text{formula weight} / n$$

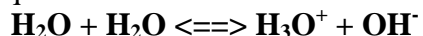
An equivalent is also defined as the equivalent weight expressed in grams. The number of equivalents in a certain mass of a substance is calculated from:

$$\text{equivalents} = \text{mass (grams) of a substance} / \text{equivalent weight (g/equiv.)}$$

Normality and molarity are related by the formula, $N = nM$, where n has the meanings stated above.

Ionization of Water

Understanding how solutes such as weak acid and bases behave in water first requires an understanding of the ions present in pure water and their interrelationships. A very small portion of the water molecules in pure liquid water react with each other as follows:



The reaction results in the formation of both an acid, H_3O^+ , whose conjugate base is H_2O and a base, OH^- , whose conjugate acid is H_2O . Water acts as both an acid and base as defined by Bronsted-Lowry. The equilibrium expression for this reaction is

The activity of H_3O^+ and OH^- in pure water have been determined experimentally to be 1.0×10^{-7} M. Now one liter of pure water basically weighs 1000g at 20°C and therefore the concentration of water is

$$(1000\text{g}/18.02(\text{M.W.}) / 1 \text{ liter} = 55.5 \text{ M}$$

pH and pOH

In dilute solution the activities of H_3O^+ and OH^- are considered to be the same as their concentrations. Therefore in dilute solutions:

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

The ion product for the ionization of water may be expressed in an equation.

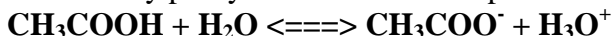
$$\log[\text{H}_3\text{O}^+] + \log[\text{OH}^-] = -14$$

therefore

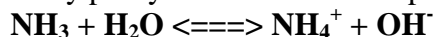
$$\text{pH} + \text{pOH} = 14$$

Weak Acids and Bases

Weak acids are acids that ionize only partly in water. An example is acetic acid.



Weak bases are bases that ionize only partly in water. An example is ammonia.



There is no clear demarcation line between strong and weak acids and between strong and weak bases. Rather there is a continuum in the strengths of each. For our purposes, the following definitions will be used:

- - weak acid - any acid that ionizes less than 10% in water at 0.5 M (for many weak acids, the percent ionization is 1 or 2%, or less). Based on this definition, weak acids have pK_a 's from 2.27 - 14.

- - weak base - any base that ionizes less than 10% in water at 0.5 M (for many, the percent ionization is 1 or 2%, or less). Based on this definition, weak bases have pK_b 's from 2.27-14.

These definitions for weak acid and base are somewhat arbitrary. There is general agreement that weak acids are those with pK_a 's between about 2 and 14, and weak bases are those with pK_b 's between about 2 and 14.

Buffers

A buffer is a solution that resists changes in pH when acid or base are added to it. A buffer consists of a solution of a weak acid and the corresponding conjugate base. One can also state it consists of a solution of a weak base and its conjugate acid. These two statements say the same thing. A buffer may be prepared from either a weak acid or a weak base. For example, a 0.05 M acetate solution at pH 5.0 is a buffer. It is prepared from acetic acid by converting some of the acetic acid to acetate ion with strong base. The conjugate weak acid/weak base pair is acetic acid/acetate ion. The word "acetate" in acetate buffer refers to both the conjugate acid (in this example, acetic acid) and the conjugate base (acetate ion). These two species together make up the acetate buffer. Each species is present in the buffer at a specific concentration and the concentration given for the acetate buffer is the sum of the concentrations of these two species, in this example 0.05 M. The ratio of the concentrations of the two species in the buffer is obtained from the Henderson-Hasselbalch equation.

How do we know what weak acid or base to select for the preparation of a buffer? First, the pH of the buffer to be prepared must be decided. This is dictated by what pH is needed in the experiment being performed. Secondly the pK_a of the weak acid of the conjugate acid/base pair should be at or near the pH to be used in the experiment. Recall from the discussion of titration curves that the pH of a solution of a weak acid changes least at the pK_a of the acid (Previous Lecture). As an example, assume the activity of an enzyme is to be tested at pH 5.0. A weak acid whose pK_a is about 5.0 should be used. Acetic acid has a pK_a of 4.77 and hence an acetate buffer can be used.

All buffers should be prepared by dissolving the appropriate weak acid (or weak base) in about 3/4 of the total volume of water needed for the buffer and adjusting the solution to the desired pH by using a pH meter and either a strong base (or acid). The solution is then quantitatively transferred to a volumetric flask and brought to volume.

How does a buffer work? Consider the acetate buffer above. When an acid (H_3O^+) is added to the buffer, a change in pH is resisted by Ac^- reacting with the acid: In this way, H_3O^+ is neutralized. But all of the added H_3O^+ is not neutralized because as neutralization occurs, the $[HAc]$ increases and the $[Ac^-]$ decreases and neutralization only continues until equilibrium is again restored. The $[H_3O^+]$ is somewhat higher in concentration at the new equilibrium because the new equilibrium concentration of Ac^- is lower. For this reason a buffer only resists changes in pH it does not completely prevent a change in pH. Buffers therefore do change in pH when an acid or base is added. They simply change much less than a solution with no buffer. When base (OH^-) is added to the acetate buffer the following reaction occurs:

Again all the added OH^- is not neutralized because the new equilibrium concentration of HAc is lower and therefore a higher concentration of OH^- is required to maintain the new equilibrium.

Buffers have maximum buffering capacity against added acid and base when equal molar quantities of the weak acid/weak base conjugate pair are present in the buffer solution. If more of the conjugate acid is present in the buffer than conjugate base, the buffer has greater buffering capacity against added bases than acids. Conversely if more conjugate base is present than conjugate/acid, the buffer has greater buffering capacity against added acid than base.