EQUIVALENTS AND NORMALITY

INTRODUCTION
Chemists often find it convenient to use “equivalents” instead of “moles” to quantify the amount of a substance. Equivalents are also used in biology, environmental science, pharmacy and other health professions. Solution concentrations of equivalents are expressed in “normality” instead of “molarity”. In this introduction to equivalents and normality, the discussion will be limited to protonic (hydrogen ion) acids and hydroxide bases in acid-base reactions. Equivalents are also used for amounts of oxidizing agents and reducing agents in redox reactions. An example of this use of equivalents and normality will be demonstrated in a laboratory experiment involving the titration of sodium oxalate with potassium permanganate.

The purpose for using equivalents instead of moles is that equivalents are defined so that one equivalent of any acid will react with one equivalent of any base. Recall that this is not true for moles. One mole of any acid will not always react with one mole of any base. Consider the following two chemical equations:

\[
\text{HCl} \quad + \quad \text{NaOH} \quad = \quad \text{NaCl} \quad + \quad \text{H}_2\text{O}
\]

In this first reaction one mole of HCl reacts with one mole of NaOH.

\[
\text{H}_2\text{SO}_4 \quad + \quad 2 \quad \text{NaOH} \quad = \quad \text{Na}_2\text{SO}_4 \quad + \quad 2 \quad \text{H}_2\text{O}
\]

In this second reaction one mole of H2SO4 reacts with two moles of NaOH.

EQUIVALENTS OF ACIDS AND BASES

Acids
An equivalent of a protonic acid is defined as the amount of the acid that will donate one mole of hydrogen ions in reactions with bases. The number of equivalents of an acid equal to one mole of the acid can be determined from its chemical formula.

a) HCl has only one acidic hydrogen. Thus one mole of HCl is equal to one equivalent (abbreviated “eq”) of HCl, since one mole of HCl donates one mole of H⁺ ions. 1 mol HCl = 1 eq HCl.

b) H₂SO₄ has two acidic hydrogens. Thus one mole of H₂SO₄ donates two moles of H⁺ ions and contains two equivalents of H₂SO₄. 1 mol H₂SO₄ = 2 eq H₂SO₄.

c) Consider acetic acid, HC₂H₃O₂. The chemical formulas for acids shows the acidic hydrogens first. There is only one acidic hydrogen in acetic acid and three non-acidic hydrogens. 1 mol HC₂H₃O₂ = 1 eq HC₂H₃O₂.

A generalized equation is: 1 mol acid = n eq acid, where n is the number of acidic hydrogens in the chemical formula for the acid.
Bases

An equivalent of an hydroxide base is defined as the amount of the base that will react with one mole of hydrogen ions. Since one mole of hydroxide ions reacts with one mole of hydrogen ions (\(H^+ + OH^- = H_2O\)), the number of equivalents of an hydroxide base in one mole of the hydroxide base equals the number of hydroxide ions in the chemical formula of the base. 

\[ 1 \text{ mol base} = n \text{ eq base}, \text{ where } n \text{ is the number of hydroxides in the chemical formula.} \]

<table>
<thead>
<tr>
<th>Base</th>
<th>Mol</th>
<th>Eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ca (OH)(_2)</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Al (OH)(_3)</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

Note that the #eq of an acid or base is > #mol of an acid or base.

To conclude this section, reconsider the balanced chemical equation for the reaction of sulfuric acid and sodium hydroxide.

\[ \text{H}_2\text{SO}_4 \ + \ 2 \text{ NaOH} \ = \ \text{Na}_2\text{SO}_4 \ + 2 \text{ H}_2\text{O} \]

1 mol \(\rightarrow\) 2 eq

We see that the #eq acid = #eq base, which is true for all acid-base reactions.

**Equivalent Weight**

One mole of a substance is defined as the weight (mass) in grams equal to its molecular weight (MW). Similarly, one equivalent of a substance is the weight in grams equal to its “equivalent weight” (EW).

\[ \text{a)} \quad \text{For HCl, } 1 \text{ mol HCl} = 1 \text{ eq HCl. MW of HCl} = 36.46; \text{ EW of HCl} = 36.46. \]

\[ \text{b)} \quad \text{For H}_2\text{SO}_4, \ 1\text{ mol } \text{H}_2\text{SO}_4 = 2 \text{ eq } \text{H}_2\text{SO}_4. \quad \text{MW of } \text{H}_2\text{SO}_4 = 98.08; \quad \text{EW of } \text{H}_2\text{SO}_4 = 49.04. \]

For acids, \(\text{EW} = \text{MW}/n\), where \(n\) is the number of acidic hydrogens in the chemical formula.

For hydroxide bases, \(\text{EW} = \text{MW}/n\), where \(n\) is the number of hydroxide ions in the chemical formula.

The EW is always less than or equal to the MW. \(\text{EW} \leq \text{MW}\).

**Molecular Weights and Equivalent Weights of some Acids and Bases**

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>EW</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO(_3)</td>
<td>63.01</td>
<td>63.01</td>
</tr>
<tr>
<td>H(_3)PO(_4)</td>
<td>98.00</td>
<td>32.67</td>
</tr>
<tr>
<td>NaOH</td>
<td>40.00</td>
<td>40.00</td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>74.09</td>
<td>37.05</td>
</tr>
<tr>
<td>Al(OH)(_3)</td>
<td>78.00</td>
<td>26.00</td>
</tr>
</tbody>
</table>
Problems Involving Equivalents

Problems involving equivalents, weights, and equivalent weights are similar to those for moles. Just as the MW was needed for mole problems, the EW is needed for problems with equivalents. There is a mathematical formula for solving these problems,

\[
\text{#eq} = \frac{wt \ (g)}{EW}.
\]

If any two of these variables are known, the third variable can be calculated.

These same problems can also be solved using dimensional analysis, using the following conversion factor:

\[
1 \text{ eq} = \frac{EW \ (g)}{1}
\]

For example, 1 eq H₂SO₄ = 49.04 g H₂SO₄

Example problem and solutions

Calculate the #eq of Ca(OH)₂ in 6.32 g of Ca(OH)₂.

\[
\text{EW}_{\text{Ca(OH)₂}} = \frac{\text{MW}_{\text{Ca(OH)₂}}}{2} = \frac{74.09}{2} = 37.05
\]

Using the formula:

\[
\text{#eq}_{\text{Ca(OH)₂}} = \frac{wt \ (g) \text{ Ca(OH)₂}}{\text{EW}_{\text{Ca(OH)₂}}}
\]

\[
\text{#eq}_{\text{Ca(OH)₂}} = \frac{6.32 \ text{ g Ca(OH)₂}}{37.05 \ text{ g Ca(OH)₂/eq Ca(OH)₂}} = 0.171 \text{ eq Ca(OH)₂}
\]

OR

Using dimensional analysis:

\[
6.32 \ text{ g Ca(OH)₂ \times 1 \text{ eq Ca(OH)₂}} = 0.171 \text{ eq Ca(OH)₂}
\]

\[
\frac{37.05 \ text{ g Ca(OH)₂}}{	ext{eq Ca(OH)₂}}
\]

NORMALITY

The “normality” (N) of a substance in solution is equal to the number of equivalents of the substance in one liter of solution.

\[
N_A = \frac{\text{#eq}_A}{\text{#L}_{\text{soln}}}
\]

Problems involving normality are similar to problems involving molarity.

Example Problem

Calculate the normality of a Ca(OH)₂ solution containing 6.32 g of Ca(OH)₂ in 5.85 L of solution.

\[
N_{\text{Ca(OH)₂}} = \frac{\text{#eq Ca(OH)₂}}{\text{#L}_{\text{soln}}}
\]
In the example above, we calculated that 6.32 g Ca(OH)\textsubscript{2} = 0.171 eq Ca(OH)\textsubscript{2}.

Thus, \( N_{\text{Ca(OH)\textsubscript{2}}} = \frac{0.171 \text{ eq Ca(OH)\textsubscript{2}}}{5.85 \text{ L soln}} = 0.0292 \text{ N} \)

The solution is said to be a 0.0292 “normal” solution of Ca(OH)\textsubscript{2}. N can stand for the noun, “normality” or the adjective, “normal”, just as M stands for molarity and molar.

**Conversion of Normality to Molarity and Molarity to Normality**

A problem that comes up frequently is to calculate the normality of a molar solution and vice versa. To keep from getting confused, remember that \#eq > \#mol, and therefore \( N > M \).

For acids, \( N = nM \), where \( n \) is the number of acidic hydrogens in the chemical formula of the acid.

For hydroxide bases, \( N = nM \), where \( n \) is the number of hydroxide ions in the chemical formula of the base.

**Examples**

6.0 M HCl = 6.0 N HCl; 3.0M H\textsubscript{2}SO\textsubscript{4} = 6.0 N H\textsubscript{2}SO\textsubscript{4}; 0.050 N Ca(OH)\textsubscript{2} = 0.025 M Ca(OH)\textsubscript{2}

**Titrations**

In calculations involving titrations, the equation, \( N_A = \frac{\#_{eq \text{ A}}}{L_{\text{soln}}} \) is used in the rearranged form, \( N_A \times L_{\text{soln}} = \#_{eq \text{ A}} \).

Titrations are reactions in which we measure the volume of a standardized solution (e.g. NaOH) that reacts stoichiometrically with an acid. In an acid-base reaction, using the concept of equivalents, we know that at the endpoint of a titration:

\( \#_{eq \text{ base}} = \#_{eq \text{ acid}} \).

**Example: Calculation of wt% of sulfuric acid by titration with NaOH**

A 0.3725 g sample of a sulfuric acid solution is titrated with 28.63 mL of a 0.1095 N NaOH solution. Calculate the wt% of sulfuric acid in the solution.

\( \#_{eq \text{ H}_2\text{SO}_4} = \#_{eq \text{ NaOH}} = N_{\text{NaOH}} \times L_{\text{soln}} \)

Thus, \( \#_{eq \text{ H}_2\text{SO}_4} = N_{\text{NaOH}} \times L_{\text{soln}} = 0.1095 \times 0.02863 = 0.003135 \text{ eq H}_2\text{SO}_4 \)

The EW of H\textsubscript{2}SO\textsubscript{4} = 98.08/2 = 49.04

\( \frac{0.003135 \text{ eq H}_2\text{SO}_4 \times 49.04 \text{ g H}_2\text{SO}_4}{1 \text{ eq H}_2\text{SO}_4} = 0.1537 \text{ g H}_2\text{SO}_4 \)
wt% $H_2SO_4 = \frac{wt\ H_2SO_4 \times 100}{wt\ sample} = \frac{0.1537\ g\ H_2SO_4 \times 100}{0.3725\ g\ sample} = 41.27\%$

This calculation routine can be written as the following equation for titrimetric analysis using normality,

$$\text{wt\% } U = \frac{N_T V_T (EW)_U \times 100}{wt\ sample}$$

where $U$ is the unknown substance and $T$ is the titrating substance. $V$ is liters. This equation is quite easy to commit to memory and then use for wt% calculations.

**Example Problem**

It took 33.6 mL of 0.225 N NaOH to titrate a 0.958 g sample of an acetic acid ($HC_2H_3O_2$) sample. Calculate the wt% of acetic acid in the sample.

$$\text{wt\% } HC_2H_3O_2 = \frac{(N_{NaOH})(V_{NaOH})(EW_{AA})(100)}{wt\ sample}$$

$$\text{MW}_{AA} = 60.05$$
$$\text{EW}_{AA} = 60.05$$

$$\text{wt\% } HC_2H_3O_2 = \frac{(0.225)(0.0336)(60.05)g \times 100}{0.958g} = 47.4\%$$

**Standardization of an Acid Solution by Titration with a Standardized Base**

HCl solutions for titrating bases are usually standardized by titration with standardized NaOH. At the titration endpoint, $\#eq \text{NaOH} = \#eq \text{HCl}$. Therefore $N_{HCl} V_{HCl} = N_{NaOH} V_{NaOH}$. The normality of the HCl can be calculated as follows.

$$N_{HCl} = N_{NaOH} \times \frac{(V_{NaOH})}{(V_{HCl})}$$

Since the conversion factor is the ratio of the volume of the NaOH to the volume of the HCl, this technique is called standardization by ratio.

**Example Problem**

It takes 32.75 mL of 0.1835N NaOH to titrate 23.42 mL of an HCl solution. Calculate the normality of the HCl solution.

$$N_{HCl} = N_{NaOH} \times \frac{(V_{NaOH})}{(V_{HCl})}$$

$$N_{HCl} = 0.1835 \times \frac{32.75}{23.42} = 0.2566N$$
PROBLEMS

1. Determine the equivalent weights of the following acids and bases:  
   a) Ca(OH)$_2$  
   b) H$_2$C$_2$O$_4$  
   c) KOH  
   d) H$_2$CO$_3$

2. How many equivalents is 15.0 g of:  
   a) H$_2$SO$_4$  
   b) Ca(OH)$_2$  
   c) Al(OH)$_3$?

3. What is the molarity of:  
   a) 0.12N H$_2$SO$_4$  
   b) 0.55N NaOH  
   c) 0.020N Ca(OH)$_2$?

4. What is the normality of:  
   a) 0.45M Al(OH)$_3$  
   b) 0.122M H$_2$SO$_4$  
   c) 0.675M H$_3$PO$_4$?

5. A 15.0 mL sample of an acid requires 37.3 mL of 0.303N NaOH for neutralization. Calculate the normality of the acid.

6. a) How many equivalents of NaOH are present in 305 mL of 0.150N NaOH?  
   b) How many equivalents of H$_2$SO$_4$ are present in 35.5 mL of 1.35N H$_2$SO$_4$?

7. A 0.243 g sample containing Ca(OH)$_2$ was titrated with 22.7 mL of a 0.109N solution of HCl. Calculate the wt% of Ca(OH)$_2$ in the sample.

8. A 0.336 g sample containing oxalic acid, H$_2$C$_2$O$_4$, was titrated with 17.7 mL of a 0.0996N NaOH solution. Calculate the wt% of oxalic acid in the sample.

Answers: 1. a) 37.05  
   b) 45.04  
   c) 56.11  
   d) 31.01:  
   2. a) 0.306 eq  
   b) 0.405 eq  
   c) 0.577 eq:  
   3. a) 0.060M  
   b) 0.55M  
   c) 0.010M;  
   4. a) 1.35N  
   b) 0.244N  
   c) 2.02N:  
   5. 0.753N  
   6. a) 0.0458 eq  
   b) 0.0479 eq  
   7. 37.7%  
   8. 23.6%